## TITLE OF THE INVENTION

## METHOD OF FORMING COLOR IMAGES

5

10

15

20

25

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is based upon and claims the benefit of priority from prior Japanese Patent Application No. 2003-051735, filed February 27, 2003, the entire contents of which are incorporated herein by reference.

## BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method of forming color images. More particularly, the present invention relates to a method of forming duplicate color images exhibiting enhanced saturation and gradation reproduction.

2. Description of the Related Art

The today widespread color photographs can be broadly classified into the color negative film, color reversal film, color instant film, etc. for shooting, and the color paper, reversal paper, display film, etc. providing prints of images recorded in the shooting materials and subjected to viewing. Among the former shooting materials, positive photosensitive materials such as a color reversal film and an instant film are dual purpose materials that are shooting materials and simultaneously can be subjected to viewing. With respect to materials for exclusive use in shooting,

print materials are absolutely needed because without corresponding print materials, viewing cannot be made. In this connection, with respect to dual purpose materials as well, print materials (duplicate materials) are needed when it is intended to store precious original images or to avoid damaging original images in, for example, processing thereof as a printing original, or when there are requirements for enlargement or use of multiple duplicates.

5

10

15

20

25

These print materials can be broadly classified into two types. The color reversal paper and color auto positive paper comprising a reflective support and subjected to viewing with reflected light, belong to the one type. The color duplicating film and display film comprising a transparent support or translucent support and subjected to viewing with transmitted light or projection, belong to the other type. Among these, the color duplicating film is demanded to have exactly the same quality as that of an original image, since the color duplicating film can be simultaneously viewed with the original image arranged sideways. Moreover, this color duplicating film may be used as an original for printing or stored as a stock photo for a prolonged period of time. Consequently, from the viewpoint of practical use as well, it is demanded to obtain a duplicate identical with the original image. However, in reality, it is extremely difficult to reproduce

exactly the same image quality because of the performance of photosensitive material, performance of printer equipment, print technology, etc.

The quality of color images is principally determined by three elements, namely, gradation reproduction, color reproduction and image quality reproduction (granularity and sharpness). Among these, the gradation reproduction is of the utmost importance for the color duplicating film demanded to realize faithful reproduction.

5

10

15

20

25

Furthermore, with respect to the color duplicating film, it is believed that the use of dupe films in printing, etc. should be minimized because of the deterioration of saturation and change of color from those of the original image with the exception that extinguishment of original images by cut-and-paste, retouch, etc. is anticipated. Accordingly, there has been a demand for improvement thereof. With respect to the color reversal paper as well, due to the deterioration of saturation and change of color from those of the original image, there has been a demand for improvement thereof.

Heretofore, with respect to tone reproduction, attempts aiming at faithful reproduction not accompanied by deterioration of the tone of original image have been conducted (see, for example, R. M. Evans, Principles of Color Photography, 1953). In this

technical literature, there are respective descriptions for the instance where the hues of color-forming dyes of a color photosensitive material for use as an original image and a color photosensitive material for print are identical with each other, and the instance where the hues are different from each other. However, the contents thereof only present an idealized discussion separately presuming the instance where the hues are identical with each other and the instance where the hues are different from each other. There is no description regarding the technique and means for simultaneously coping with the two instances.

As means for solving these, there has been proposed a method of regulating the wavelength of maximum sensitivity in the spectral sensitivity distribution of each color sensitive layer and regulating the point gamma of characteristic curve thereof (see, for example, Jpn. Pat. Appln. KOKAI Publication No. (hereinafter referred to as JP-A-) 9-222702). This method includes special device with respect to the spectral sensitivity of especially a red sensitive layer but is for the external system (system in which color couplers are supplied from processing solutions) whose market share is now substantially nil. In the current situation wherein the market share is substantially entirely occupied by the internal system (system in which color couplers are incorporated in

photosensitive materials), the tone reproduction is unsatisfactory.

5

10

15

20

25

Further, in recent years, cyan couplers and magenta couplers having unfavorable absorptions reduced have been developed, and studies have been conducted for enhancing the color reproduction of photosensitive materials for shooting (see, for example, JP-A-2001-142181). Still further, the method of forming color images with the use of the same cyan coupler and same magenta coupler having unfavorable absorptions reduced in both a photosensitive material for shooting and a photosensitive material for duplication is known (see, for example, JP-A-9-222710). Desirable tone reproduction cannot be attained by this method, and hence improvements are demanded.

## BRIEF SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method of forming a duplicate color image exhibiting enhanced saturation and enhanced gradation reproduction. It is an especial object of the present invention to provide a method of forming a faithful duplicate image with respect to transmission type color reversal photosensitive materials.

The inventor has found that the objects of the present invention can be attained by the following means.

(1) A method of forming color images, comprising

forming an original image on an image-forming material and duplicating the formed original image on a color photosensitive material for use in the duplication, the color photosensitive material for use in the duplication comprising at least one blue-sensitive silver halide emulsion layer containing a yellow coupler, at least one green-sensitive silver halide emulsion layer containing a magenta coupler and at least one red-sensitive silver halide emulsion layer containing a cyan coupler on a support of a transmission-type or reflection-type, wherein the formed original image contains a dye formed from a cyan coupler selected from among compounds represented by the following general formula (CC-1), and wherein with respect to the red-sensitive silver halide emulsion layer of the color photosensitive material for use in the duplication, the maximum sensitivity wavelength, Amax (D), of spectral sensitivity distribution at each density satisfies the relationship:

630 nm  $\leq \lambda \max$  (D)  $\leq$  670 nm.

5

10

15

20

25

$$\begin{array}{c}
R_{11} \\
Y \\
N \\
NH \\
G_a = G_b
\end{array}$$
(CC-1)

In the general formula (CC-1), Ga represents  $-C(R_{13}) = \text{ or } -N = ;$  Gb represents  $-C(R_{13}) = \text{ when}$  Ga represents -N =, or Gb represents -N = when Ga

represents  $-C(R_{13})=$ ; each of  $R_{11}$  and  $R_{12}$  represents an electron-withdrawing group having a Hammett substituent constant  $\sigma p$  value of 0.20 to 1.0;  $R_{13}$  represents a substituent; Y represents a hydrogen atom or a group capable of splitting-off by a coupling reaction with an oxidized product of an aromatic primary amine color developing agent.

5

10

15

- (2) The method of forming color images according to item (1) above, wherein the color photosensitive material for use in the duplication contains a cyan coupler selected from among compounds represented by the above general formula (CC-1).
- (3) The method of forming color images according to item (1) or (2) above, wherein the color photosensitive material for use in the duplication contains a magenta coupler selected from among compounds represented by the following general formula (MC-1):

In formula (MC-1),  $R_1$  represents a hydrogen atom or substituent; one of  $G_1$  and  $G_2$  represents a carbon atom, and the other represents a nitrogen atom; and  $R_2$  represents a substituent that substitutes one of  $G_1$  and  $G_2$  which is a carbon atom.  $R_1$  and  $R_2$  may further have

a substituent, or a polymer chain may be bonded to the magenta coupler via  $R_1$  or  $R_2$ . X represents a hydrogen atom or a group capable of splitting-off by a coupling reaction with an oxidized product of an aromatic primary amine color developing agent.

5

10

15

20

(4) The method of forming color images according to any of items (1) to (3) above, wherein the color photosensitive material for use in the duplication contains a yellow coupler selected from among compounds represented by the following general formula (YC-1):

In this formula, Q represents a nonmetallic atomic group capable of forming a 5- to 7-membered ring in cooperation with -N=C-N(R1)-. R1 represents a substituent. R2 represents a substituent. m is an integer of 0 to 5. When m is 2 or greater, two or more R2s may be identical with or different from each other, and may be bonded with each other to thereby form a ring. X represents a hydrogen atom or a group capable of splitting-off by a coupling reaction with an oxidation product of a developing agent.

Additional objects and advantages of the invention will be set forth in the description which follows, and

4

5

10

15

20

25

in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out hereinafter.

DETAILED DESCRIPTION OF THE INVENTION

The couplers preferably used in the present invention will be described in detail below.

Firstly, the coupler represented by the general formula (CC-1) will be described.

In the general formula (CC-1), Ga represents  $-C(R_{13}) = \text{ or } -N =$ ; Gb represents  $-C(R_{13}) = \text{ when}$  Ga represents -N =, or Gb represents -N = when Ga represents  $-C(R_{13}) =$ ; Y represents a hydrogen atom or a group capable of splitting-off by a coupling reaction with an oxidized product of an aromatic primary amine color developing agent (hereinafter also referred to as "a split-off group"). Each of  $R_{11}$  and  $R_{12}$  represents an electron-withdrawing group having a Hammett substituent constant  $\sigma p$  value of 0.20 to 1.0.  $R_{13}$  represents a substituent.

Although both  $R_{11}$  and  $R_{12}$  represent an electron-withdrawing group having a Hammett substituent constant  $\sigma p$  value of 0.20 to 1.0, the sum of the  $\sigma p$  values of  $R_{11}$  and  $R_{12}$  is desirably 0.65 or more. The coupler of the invention is given superior performance as a cyan coupler by introducing this strong electron-withdrawing

group. The sum of the  $\sigma p$  values of R<sub>11</sub> and R<sub>12</sub> is preferably 0.70 or more, and its upper limit is about 1.8.

5

10

15

20

25

In the invention, each of  $R_{11}$  and  $R_{12}$  is an electron-withdrawing group with a Hammett substituent constant  $\sigma p$  value (hereinafter also referred to as "a  $\sigma p$  value") of 0.20 to 1.0. Preferably each of  $R_{11}$  and  $R_{12}$  is an electron-withdrawing group having a  $\sigma p$  value of 0.30 to 0.8.

The Hammett's rule is an empirical rule proposed by L.P. Hammett in 1935 in order to quantitatively arque the effects of substituents on reaction or equilibrium of benzene derivatives. The rule is widely regarded as appropriate in these days. The substituent constants obtained by the Hammett rule include a  $\sigma p$ value and a  $\sigma m$  value, and these values are described in a large number of general literature. For example, the values are described in detail in J. A. Dean ed., "Lange's Hand Book of Chemistry," the 12th edition, 1979 (McGraw-Hill), "The Extra Number of The Domain of Chemistry, "Vol. 122, pages 96 to 103, 1979 (Nanko Do) and Chemical Reviews, vol. 91, pp.165-195 (1991), the disclosures of which are incorporated herein by reference. In the invention, each of  $R_{11}$  and  $R_{12}$  is defined by the Hammett substituent constant  $\sigma p$  value. However, this does not mean that  $R_{11}$  and  $R_{12}$  are limited to substituents having the already known values Ų

5

10

15

20

25

described in these literature. That is, the invention includes, of course, substituents having values that fall within the above range when measured on the basis of the Hammett's rule even if they are unknown in literature.

Practical examples of  $R_{11}$  and  $R_{12}$ , as the electron-withdrawing group with a σp value of 0.20 to 1.0, are an acyl group, acyloxy group, carbamoyl group, aliphatic oxycarbonyl group, aryloxycarbonyl group, cyano group, nitro group, dialkylphosphono group, diarylphosphono group, diarylphosphinyl group, alkylsulfinyl group, arylsulfinyl group, alkylsulfonyl group, arylsulfonyl group, sulfonyloxy group, acylthio group, sulfamoyl group, thiocyanate group, thiocarbonyl group, alkyl group substituted by at least two halogen atoms, alkoxy group substituted by at least two halogen atoms, aryloxy group substituted by at least two halogen atoms, alkylamino group substituted by at least two halogen atoms, alkylthio group substituted by at least two halogen atoms, aryl group substituted by another electron-withdrawing group with a  $\sigma p$  value of 0.20 or more, heterocyclic group, chlorine atom, bromine atom azo group, and selenocyanate group. Of these substituents, those capable of further having substituents can further have substitutes to be mentioned later for R13.

The aliphatic portion of the aliphatic oxycarbonyl

group can be straight-chain, branched-chain, or cyclic and can be saturated or can contain an unsaturated bond. This aliphatic oxycarbonyl group includes, e.g., alkoxycarbonyl, cycloalkoxycarbonyl, alkenyloxycarbonyl, alkinyloxycarbonyl, and cycloalkenyloxycarbonyl.

5

10

15

20

25

The  $\sigma p$  values of representative electronwithdrawing groups having a σp value of 0.2 to 1.0 are a bromine atom (0.23), chlorine atom (0.23), cyano group (0.66), nitro group (0.78), trifluoromethyl group (0.54), tribromomethyl group (0.29), trichloromethyl group (0.33), carboxyl group (0.45), acetyl group (0.50), benzoyl group (0.43), acetyloxy group (0.31), trifluoromethanesulfonyl group (0.92), methanesulfonyl group (0.72), benzenesulfonyl group (0.70), methanesulfinyl group (0.49), carbamoyl group (0.36), methoxycarbonyl group (0.45), ethoxycarbonyl group (0.45), phenoxycarbonyl group (0.44), pyrazolyl group (0.37), methanesulfonyloxy group (0.36), dimethoxyphosphoryl group (0.60), and sulfamoyl group (0.57). Each of the numbers in parenthesis is  $\sigma p$  value.

R<sub>11</sub> preferably represents a cyano group, aliphatic oxycarbonyl group (a 2- to 36-carbon, straight-chain or branched-chain alkoxycarbonyl group, aralkyloxycarbonyl group, alkenyloxycarbonyl group, alkinyloxycarbonyl group, cycloalkoxycarbonyl group, or

0

è, ai é.

> cycloalkenyloxycarbonyl group, e.g., methoxycarbonyl, ethoxycarbonyl, dodecyloxycarbonyl, octadecyloxycarbonyl, 2-ethylhexyloxycarbonyl, sec-butyloxycarbonyl, oleyloxycarbonyl, 5 benzyloxycarbonyl, propargyloxycarbonyl, cyclopentyloxycarbonyl, cyclohexyloxycarbonyl, or 2,6-di-t-butyl-4-methylcylohexyloxycarbonyl); dialkylphosphono group (a 2- to 36-carbon dialkylphosphono group, e.g., diethylphosphono or dimethylphosphono); alkylsulfonyl or arylsulfonyl group 10 (a 1- to 36-carbon alkylsulfonyl or 6- to 36-carbon arylsulfonyl group, e.g., a methanesulfonyl group, butanesulfonyl group, benzenesulfonyl group, or p-toluenesulfonyl group); or fluorinated alkyl group 15 (a 1- to 36-carbon fluorinated alkyl group, e.g., trifluoromethyl).  $R_{11}$  is particularly preferably a cyano group, aliphatic oxycarbonyl group, or fluorinated alkyl group, and most preferably, a cyano group.

> 20 R<sub>12</sub> preferably represents an aliphatic oxycarbonyl group as mentioned above for R<sub>11</sub>; carbamoyl group (a 1- to 36-carbon carbamoyl group, e.g., diphenylcarbamoyl or dioctylcarbamoyl); sulfamoyl group (a 1- to 36-carbon sulfamoyl, e.g., dimethylsulfamoyl or dibutylsulfamoyl); dialkylphosphono group mentioned above for R<sub>11</sub>; diarylphosphono group (a 12- to 50-carbon diarylphosphono group, e.g.,

diphenylphosphono or di(p-tolyl)phosphono).  $R_{12}$  is particularly preferably a group represented by the following formula (Z):

$$R_{4}'$$

$$R_{5}'$$

$$R_{2}'$$

$$(Z)$$

In the formula (X), each of R<sub>1</sub>' and R<sub>2</sub>' represents an aliphatic group, e.g., a 1- to 36-carbon, straight-chain or branched-chain alkyl group, aralkyl group, alkenyl group, alkinyl group, cycloalkyl group, or cycloalkenyl group, and more specifically, methyl, ethyl, propyl, isopropyl, t-butyl, t-amyl, t-octyl, tridecyl, cyclopentyl, cyclohexyl, vinyl allyl, 1-propenyl, or 2-pentenyl. Each of R<sub>3</sub>', R<sub>4</sub>' and R<sub>5</sub>' represents a hydrogen atom or aliphatic group.

Examples of the aliphatic group are those mentioned above for R<sub>1</sub>' and R<sub>2</sub>'. Each of R<sub>3</sub>', R<sub>4</sub>', and R<sub>5</sub>' is preferably a hydrogen atom.

W represents a non-metallic atomic group required to form a 5- to 8-membered ring. This ring may be substituted, may be a saturated ring, or can have an unsaturated bond. A non-metallic atom is preferably a nitrogen atom, oxygen atom, sulfur atom, or carbon atom, and more preferably, a carbon atom.

20

Examples of a ring formed by W are a cyclopentane

6

5

10

15

20

25

ring, cyclohexane ring, cycloheptane ring, cyclooctane ring, cyclohexene ring, piperazine ring, oxane ring, and thiane ring. These rings can be substituted by a substituents represented by  $R_{13}$  to be described below.

A ring formed by W is preferably a cyclohexane ring which may be substituted, and most preferably, a cyclohexane ring whose 4-position is substituted by a 1- to 36-carbon alkyl group (which may be substituted by a substituent represented by  $R_{13}$  to be described below).

 $R_{13}$  represents a substituent. Examples are those mentioned above for  $R_2$  in formula (MC-1).

Among the substituents,  $R_{13}$  is preferably an alkyl group, aryl group, alkoxy group, aryloxy group, alkylthio group, ureido group, urethane group, or acylamino group.

Y represents a hydrogen atom or a group capable of splitting-off when the coupler reacts with an aromatic primary amine color developing agent in an oxidized form. When Y represents a split-off group, examples are those to be described lator in the explanation of X of the general formula (MC-1).

Y is preferably a hydrogen atom, halogen atom, aryloxy group, heterocyclic acyloxy group, dialkylphosphonooxy group, arylcarbonyloxy group, arylsulfonyloxy group, alkoxycarbonyloxy group, or carbamoyloxy group. Also, it is also preferable that

the split-off group or a compound released from the split-off group has a property of further reacting with an aromatic primary amine color developing agent in an oxidized form. For example, the split-off group is a non-color-forming coupler, hydroquinone derivative, aminophenol derivative, sulfonamidophenol derivative. In the present invention, Y is preferably a hydrogen atom, halogen atom or carbamoyloxy group.

5

10

15

20

25

The coupler represented by the general formula (CC-1) may be in a form of a dimer or higher polymer wherein the group represented by  $R_{12}$  or  $R_{13}$  has a residue of the coupler represented by the general formula (CC-1). The coupler represented by the general formula (CC-1) may be in a homopolymer or copolymer wherein the group represented by  $R_{12}$  or  $R_{13}$  has a polymer chain. A typical example of the homopolymer or copolymer containing the polymer chain is a homopolymer or copolymer of an addition polymerized ethylenic unsaturated compounds having the coupler residde represented by the general formula (CC-1). case, one or more kinds of cyan color-forming repeating unit having the coupler residue represented by the general formula (CC-1) may be contained in the polymer. The copolymer may be one having, as copolymerization component, one or more non-color-forming ethylenic monomer that does not couple with an aromatic primary amine developing agent in an oxidized form, such as

acrylic ester, methacrylic ester and maleic ester. The number of repeating units in the polymer is preferably 100-1000.

As preferred examples of the cyan couplers represented by the general formula (CC-1), there can be mentioned those of the following general formula (CC-2):

NC COO 
$$\stackrel{R_1'}{W}$$
NN NH  $\stackrel{R_2'}{R_2}$ 
(CC-2)

٣,

5

10

15

20

In the general formula (CC-2),  $R_{14}$  represents a substituent other than a hydrogen atom. p is a natural number of 1 to 5, and when p is 2 or greater, two or more  $R_{14}$ s may be wholly identical with or different from each other.  $R_{1}$ ',  $R_{2}$ ',  $R_{3}$ ',  $R_{4}$ ' and  $R_{5}$ ' are as defined above with respect to the general formula (Z) mentioned in the description of  $R_{12}$  of the general formula (CC-1). Y has the same meaning as that of the general formula (CC-1).

The general formula (CC-2) will be described below. As examples of the substituents represented by  $R_{14}$ , there can be mentioned those set forth with respect to  $R_{13}$  of the general formula (CC-1). Preferred examples of the substituents represented by  $R_{14}$  include a chlorine atom, fluorine atom, alkyl

4

25

group, alkoxy group, amino group, alkylthio group, arylthio group, aryloxy group, acylamino group, sulfonylamino group, carbamoyl group, sulfamoyl group, carbonyloxy group, oxycarbonyl group, ureido group, 5 oxycarbonylamino group, aminocarbonyloxy group, carboxyl group, cyano group and heterocycle group. When p is 2 or greater, at least one of the  $R_{14}s$  is preferably a substituent whose total number of carbon atoms is in the range of 6 to 80, more preferably 10 an alkyl group, alkoxy group, acylamino group, sulfonylamino group, carbamoyl group, sulfamoyl group, carbonyloxy group, oxycarbonyl group, aminocarbonylamino group, oxycarbonylamino group or aminocarbonyloxy group whose total number of carbon 15 atoms is in the range of 6 to 80 (still more preferably the total number of carbon atoms is in the range of 10 to 60). When  $R_{14}$  is a group whose total number of carbon atoms is in the range of 6 to 80, the substitution position thereof is preferably meta or 20 para, more preferably meta, to the pyrrolotriazole moiety on the phenyl group of the general formula (CC-2).

The most preferred couplers represented by the general formula (CC-2) are those wherein each of  $R_1$ 'and  $R_2$ ' is a tertiary alkyl group; each of  $R_3$ ',  $R_4$ ' and  $R_5$ ' is a hydrogen atom; the ring formed by W is a cyclohexane ring; p is 2 or 3; and at least one of the

R<sub>14</sub>s is a group selected from among an alkoxy group, acylamino group, sulfonylamino group, carbamoyl group, sulfamoyl group, carbonyloxy group, oxycarbonyl group, aminocarbonylamino group, oxycarbonylamino group and aminocarbonyloxy group whose total number of carbon atoms is in the range of 10 to 60. Among these couplers, those having a substituent on the phenyl group at the meta position to the pyrrolotriazole moiety and having a substituent of an alkoxy group, aryloxy group or amino group on the phenyl group at the para position to the pyrrolotriazole moiety are preferred. As the substituent at the para position, amino is most preferred. Y is preferably a hydrogen atom, halogen atom or carbamoyloxy group.

Specific examples of the couplers of the general formula (CC-1) will be shown below, which should not be construed as limiting the scope of the present invention.

3.

₹.

4,

•

CC-26

٤.,

CC-27 
$$t-Bu$$
  $CH_3$   $O_2N$   $O_2N$   $O_3N$   $O_4N$   $O_4N$   $O_5N$   $O_5N$   $O_5N$   $O_7N$   $O_8N$   $O$ 

The compound represented by the general

formula (CC-1) of the invention may be synthesized by known methods such as those described, for example, in J. C. S., 1961, page 518; J.C.S., 1962, page 5149;

Angew. Chem., vol. 72, page 956 (1960) and Berichte, vol. 97, page 3436 (1964) or methods cited therein or analogous methods.

Next, the magenta image-forming dye of the present will be explained below.

In the formula (MC-1),  $R_1$  represents a hydrogen atom or substituent; one of  $G_1$  and  $G_2$  represents a carbon atom, and the other represents a nitrogen atom; and  $R_2$  represents a substituent that substitutes one of  $G_1$  and  $G_2$  which is a carbon atom.  $R_1$  and  $R_2$  may

15

٠,

further have a substituent, a polymer of the general formula (MX-1) may be formed or a polymer chain may be bonded to the magenta coupler via  $R_1$  or  $R_2$ . X represents a hydrogen atom or a split-off group.

The general formula (MC-1) will be described in detail. In the formula, R<sub>1</sub> represents a hydrogen atom or a substituent selected from an alkyl group, aralkyl group, aryl group, alkoxy group, aryloxy group, amino group, acylamino group, arylthio group, alkylthio group, ureido group, alkoxycarbonylamino group, carbamoyloxy group, and heterocyclic thio group, all of which may have a substituent.

Examples of the substituent represented by R<sub>1</sub> can be an alkyl group (e.g., methyl, ethyl, isopropyl, 15 t-butyl, t-amyl, adamantly, 1-methylcyclopropyl, n-octyl, cyclohexyl, 2-methanesulfonylethyl, 3-(3-pentadecylphenoxy) propyl, 3-{4-{2-[4-(4hydroxyphenylsulfonyl)phenoxy]dodecanamide}phenyl}propyl, 20 2-ethoxytridecyl, trifluoromethyl, cyclopentyl, and 3-(2,4-di-t-amylphenoxy)propyl); aralkyl group (e.g., benzyl, 4-methoxybenzyl, and 2-methoxybenzyl); aryl group (e.g., phenyl, 4-t-butylphenyl, 2,4-di-t-amylphenyl, and 4-tetradecanamidophenyl); 25 alkoxy group (e.g., methoxy, ethoxy, 2-methoxyethoxy, 2-dodecylethoxy, 2-methanesulfonylethoxy, and 2-phenoxyethoxy); aryloxy group (e.g., phenoxy,

2-methylphenoxy, 4-t-butylphenoxy, 3-nitrophenoxy, 3-t-butyloxycarbamoylphenoxy, and 3-methoxycarbamoylphenoxy); amino group (including an anilino group, e.g., methylamino, ethylamino, anilino, dimethylamino, diethylamino, t-butylamino, 5 2-methoxyanilino, 3-acetylaminoanilino, and cyclohexylamino); acylamino group (e.g., acetamido, benzamido, tetradecanamido, 2-(2,4-di-t-amylphenoxy) butanamido, 4-(3-t-butyl-4-hydroxyphenoxy) butanamido, and 10 2-{4-(4-hydroxyphenylsulfonyl)phenoxy}decanamido); ureido group (e.g., phenylureido, methylureido, and N, N-dibutylureido); alkylthio group (e.g., methylthio, octylthio, tetradecylthio, 2-phenoxyethylthio, 15 3-phenoxypropylthio, and 3-(4-t-butylphenoxy)propylthio); arylthio group (e.g., phenylthio, 2-butoxy-5-t-octylphenylthio, 3-pentadecylphenylthio, 2-carboxyphenylthio and 4-tetradecanamidephenylthio); alkoxycarbonyamino group 20 (e.g., methoxycarbonylamino, and tetradecyloxycarbonyamino); carbamoyloxy group (e.g., N-methylcarbamoyloxy, and N-phenylcarbamoyloxy); heterocyclic thio group (e.g., 2-benzothiazolyl thio, 2,4-di-phenoxy-1,3,5-triazole-6-thio, and 25 2-pyridylthio).

Among the above-mentioned groups, alkyl group, aralkyl group, aryl group, alkoxy group, aryloxy group,

and amino group are preferable. More preferably, secondary alkyl and tertiary alkyl groups each having a total of 3- to 15-carbon, and most preferably a 4-to 10-carbon tertiary alkyl group.

5 X represents a hydrogen atom or a split-off group capable of leaving upon a coupling reaction with an aromatic primary amine color developing agent in an oxidized form. Specifically, the split-off group includes a halogen atom, alkoxy group, aryloxy group, 10 acyloxy group, alky- or aryl-sulfonyloxy group, acylamino group, alkyl- or aryl-sulfonylamido group, alkoxycarbonyloxy group, aryloxycarbonyloxy group, alkyl-, aryl-, or heterocyclic-thio group, carbamoylamino group, carbamoyloxy group, 5- or 6-15 memebered nitrogen-containing heterocyclic group, imido group, and arylazo group. These groups may be further substituted with the substituents represented by  $R_2$ .

More specifically, examples of X are a halogen atom (e.g., a fluorine atom, chlorine atom, and bromine atom); alkoxy group (e.g., ethoxy, dodecyloxy, methoxyethylcarbamoylmethoxy, carboxypropyloxy, methylsulfonylethoxy, and ethoxycarbonylmethoxy); aryloxy group (e.g., 4-methylphenoxy, 4-chlorophenoxy, 4-methoxyphenoxy, 4-carboxyphenoxy, 4-carboxyphenoxy, 4-carboxyphenoxy,

4-methoxycarboxyphenoxy, 4-carbamoylphenoxy,
3-ethoxycarboxyphenoxy, 3-acetylaminophenoxy, and
2-carboxyphenoxy); acyloxy group (e.g., acetoxy,

20

٤.

tetradecanoyloxy, and benzoyloxy); alkyl- or aryl-sulfonyloxy group (e.g., methanesulfonyloxy and toluenesulfonyloxy); acylamino group (e.g., dichloroacetylamino and heptafluorobutylylamino), 5 alkyl- or aryl-sulfonamido group (e.g., methanesulfonamido, trifluoromethanesulfonamido, and p-toluenesulfonylamido); alkoxycarbonyloxy group (e.g., ethoxycarbonyloxy and benzyloxycarbonyloxy); aryloxycarbonyloxy group (e.g., phenoxycarbonyloxy); 10 alkyl-, aryl-, or heterocyclic-thio group (e.g., dodecylthio, 1-carboxydodecylthio, phenylthio, 2-butoxy-5-t-octylphenylthio, and tetrazolylthio); carbamoylamino group (e.g., N-methylcarbamoylamino and N-phenylcarbamoylamino); carbamoyloxy group (e.g., 15 N, N-dimethylcarbamoyloxy, N-phenylcarbamoyloxy, morpholinylcarbamoyloxy, and pyrrolidinylcarbamoyloxy); 5- or 6-membered nitrogen-containing heterocyclic group (e.g., imidazolyl, pyrazolyl, triazolyl, tetrazolyl, and 1,2-dihydro-2-oxo-1-pyridyl); imido group (e.g., 20 succinimido and hydantoinyl); and arylazo group (e.g., phenylazo and 4-methoxyphenylazo). X can also take the form of a bis coupler obtained by condensing a 4-equivalent coupler by aldehydes or ketones, as a split-off group bonded via a carbon atom.

X is preferably a hydrogen atom, halogen atom, alkoxy group, aryloxy group, alkyl- or aryl-thio group, or 5- or 6-membered nitrogen-containing heterocyclic group that is bonded to the coupling active position via the nitrogen atom, and particularly preferably, a hydrogen atom, chlorine atom, or phenoxy group that may be substituted.

One of  $G_1$  and  $G_2$  is a nitrogen atom, and the other is a carbon atom.  $R_2$  in the formula (MC-1) is bonded to one of  $G_1$  and  $G_2$  which is a carbon atom.

5

10

15

20

25

R2 represents a substituent. Examples are a halogen atom, aliphatic group, aryl group, heterocyclic group, cyano group, hydroxyl group, nitro group, carboxyl group, amino group, alkoxy group, aryloxy group, acylamino group, alkylamino group, anilino group, ureido group, sulfamoylamino group, alkylthio group, arylthio group, alkoxycarbonylamino group, sulfonamido group, carbamoyl group, sulfamoyl group, sulfonyl group, alkoxycarbonyl group, heterocyclic oxy group, azo group, acyloxy group, carbamoyloxy group, silyloxy group, aryloxycarbonylamino group, imido group, heterocyclic thio group, sulfinyl group, phosphonyl group, aryloxycarbonyl group, acyl group, and azolyl group. These substituents may have a substituent.

More specifically, examples of a substituent represented by R<sub>2</sub> are a halogen atom (e.g., a chlorine atom and bromine atom); alkyl group (e.g., a 1- to 32-carbon, straight-chain or branched-chain alkyl group, aralkyl group, alkenyl group, alkinyl group,

```
cycloalkyl group and cycloalkenyl group; more
       specifically, methyl, ethyl, propyl, isopropyl,
       t-butyl, tridecyl, 2-methanesulfonylethyl,
       3-(3-pentadecylphenoxy) propyl,
 5
       3-{4-{2-[4-(4-hydroxyphenylsulfonyl)phenoxy]dodecanamid
       o}phenyl}propyl, 2-ethoxytridecyl, trifluoromethyl,
       cyclopentyl, and 3-(2,4-di-t-amylphenoxy)propyl); aryl
       group (e.g., phenyl, 4-t-butylphenyl,
       2,4-di-t-amylphenyl, and 4-tetradecanamidophenyl);
10
       heterocyclic group (e.g., 2-furyl, 2-thienyl,
       2-pyrimidinyl, and 2-benzothiazolyl); cyano group;
       hydroxyl group; nitro group; carboxyl group; amino
       group; alkoxy group (e.g., methoxy, ethoxy,
       2-methoxyethoxy, 2-dodecylethoxy, and
15
       2-methanesulfonylethoxy); aryloxy group (e.g., phenoxy,
       2-methylphenoxy, 4-t-butylphenoxy, 3-nitrophenoxy,
       3-t-butyloxycarbamoylphenoxy, and
       3-methoxycarbamoylphenoxy); acylamino group
       (e.g., acetamido, benzamido, tetradecanamido,
20
       2-(2,4-di-t-amylphenoxy) butanamido,
       4-(3-t-butyl-4-hydroxyphenoxy) butanamido,
       2-{4-(4-hydroxyphenylsulfonyl)phenoxy}decanamido);
       alkylamino group (e.g., methylamino, butylamino,
       dodecylamino, diethylamino, and methylbutylamino);
25
       anilino group (e.g., phenylamino, 2-chloroanilino,
       2-chloro-5-tetradecanaminoanilino,
       2-chloro-5-dodecyloxycarbonylanilino, N-acetylanilino,
```

and 2-chloro-5-{ $\alpha$ -(3-t-butyl-4-hydroxyphenoxy) dodecanamido anilino); ureido group (e.g., phenylureido, methylureido, and N, N-dibutylureido); sulfamoylamino group 5 (e.g., N,N-dipropylsulfamoylamino and N-methyl-N-decylsulfamoylamino); alkylthio group (e.g., methylthio, octylthio, tetradecylthio, 2-phenoxyethylthio, 3-phenoxypropylthio, and 3-(4-t-butylphenoxy)propylthio); arylthio group 10 (e.g., phenylthio, 2-butoxy-5-t-octylphenylthio, 3-pentadecylphenylthio, 2-carboxyphenylthio, and 4-tetradecanamidophenylthio); alkoxycarbonylamino group (e.g., methoxycarbonylamino and tetradecyloxycarbonylamino); sulfonamido group 15 (e.g., methanesulfonamido, hexadecanesulfonamido, benzenesulfonamido, p-toluenesulfonamido, octadecanesulfonamido, and 2-methyloxy-5-t-butylbenzenesulfonamido); carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl, 20 N-(2-dodecyloxyethyl)carbamoyl, N-methyl-N-dodecylcarbamoyl, and N-(3-(2,4-di-t-amylphenoxy)propyl)carbamoyl); sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-(2-dodecyloxyethyl) sulfamoyl, 25 N-ethyl-N-dodecylsulfamoyl, and N, N-diethylsulfamoyl); sulfonyl group (e.g., methanesulfonyl, octanesulfonyl, benzenesulfonyl, and toluenesulfonyl); alkoxycarbonyl

٠.

group (e.g., methoxycarbonyl, butyloxycarbonyl, dodecyloxycarbonyl, and octadecyloxycarbonyl); heterocyclic oxy group (e.g., 1-phenyltetrazole-5-oxy and 2-tetrahydropyranyloxy); azo group (e.g., 5 phenylazo, 4-methoxphenylazo, 4-pyvaloylaminophenylazo, and 2-hydroxy-4-propanoylphenylazo); acyloxy group (e.g., acetoxy); carbamoyloxy group (e.g., N-methylcarbamoyloxy and N-phenylcarbamoyloxy); silyloxy group (e.g., trimethylsilyloxy and 10 dibutylmethylsilyloxy); aryloxycarbonylamino group (e.g., phenoxycarbonylamino); imido group (e.g., N-succinimido, N-phthalimido, and 3-octadecenylsuccinimido); heterocyclic thio group (e.g., 2-benzothiazolylthio, 15 2,4-di-phenoxy-1,3,5-trizole-6-thio, and 2-pyridylthio); sulfinyl group (e.g., dodecanesulfinyl, 3-pentadecylphenylsulfinyl, and 3-phenoxypropylsulfinyl); phosphonyl group (e.g., phenoxyphosphonyl, octyloxyphosphonyl, and 20 phenylphosphonyl); aryloxycarbonyl group (e.g., phenoxycarbonyl); acyl group (e.g., acetyl, 3-phenylpropanoyl, benzoyl, and 4-dodecyloxybenzoyl); and azolyl group (e.g., imidazolyl, pyrazolyl, 3-chloro-pyrazole-1-yl, and triazole). 25 In a case where a group represented by R2 can

further have a substituent, such further substituent

may be an organic substituent that is bonded to R2 via

a carbon atom, oxygen atom, nitrogen atom, or sulfur atom thereof, or a halogen atom.

5

10

15

20

25

Preferable substituents as  $R_2$  are an alkyl group, aryl group, alkoxy group, aryloxy group, alkylthio group, ureido group, alkoxycarbonylamino group, and acylamino group. More preferably,  $R_2$  is a group having the total carbon atoms of 6 to 70 and having an alkyl group or aryl group as a partial structure thereof, thereby providing immobility to the coupler represented by the general formula (MC-1). Herein, the terms " $R_2$  has an alkyl group or aryl group as a partial structure thereof" include the cases where  $R_2$  is a substituent having an alkyl group or aryl group as a further substituent thereof, and also where  $R_2$  itself is an alkyl group or aryl group. The same can be applied to groups other than  $R_2$ .

Formula (MC-1) is more preferably a compound in which  $R_2$  is a substituent represented by the following general formula (BL-1) or (BL-2) below:

$$R_3$$
 $R_4$ 
 $R_5$ 
 $R_7$ 
 $R_6$ 
 $R_6$ 
 $R_8$ 
(BL-1)
(BL-2)

In the general formula (BL-1), each of  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$  and  $R_7$  independently represents a hydrogen atom or

٤.

5

10

15

20

25

a substituent, and at least one of them represents a substituent having the total carbon atoms of 4 to 70 and containing a substituted or unsubstituted alkyl group as a partial structure thereof, or a substituent having the total carbon atoms of 6 to 70 and containing a substituted or unsubstituted aryl group as a partial structure thereof.

A group represented by the general formula (BL-1) will be described below. Each of R3, R4, R5, R6, and R7 independently represents a hydrogen atom or a substituent. Examples of the substituent are those enumerated above for R2. At least one of R3, R4, R5,  $R_6$ , and  $R_7$  is a substituent having the total carbon atoms of 4 to 70 and containing a substituted or unsubstituted alkyl group as a partial structure thereof, or a substituent having the total carbon atoms of 6 to 70 and containing a substituted or unsubstituted aryl group as a partial structure thereof. Preferred examples are an alkoxy group, aryloxy group, acylamino group, ureido group, carbamoyl group, alkoxycarbonylamino group, sulfonyl group, sulfonamido groups, sulfamoyl group, sulfamoylamino group, and alkoxycarbonyl group, each containing a substituted or unsubstituted alkyl or aryl group as a partial structure thereof, and an alkyl group and aryl group, each having the total carbon atoms of 4 (6 if an aryl group is contained) to 70. Of these substituents,

٠,

5

an alkyl group having 4 to 70 carbon atoms, and an alkoxy group, acylamino group and sulfonamido groups each having an alkyl group having 4 to 70 carbon atoms as a partial structure thereof are preferred.

Especially preferably,  $R_3$ , or both of  $R_4$  and  $R_6$  represent a substituent having the total carbon atoms of 4 (6 if aryl group is contained) to 70, and having a substituted or unsubstituted alkyl or aryl group as a partial structure thereof.

10 In the general formula (BL-2), G<sub>3</sub> represents a substituted or unsubstituted methylene group; a represents an integer from 1 to 3; Rg represents a hydrogen atom, alkyl group, or aryl group; G4 represents -O- or -SO2-; and R9 represents 15 a substituent having the total carbon atoms of 6 to 70 and containing a substituted or unsubstituted alkyl or aryl group as a partial structure thereof. If Ro has a substituent, examples of this substituent are those enumerated above for R2. If a is 2 or more, 20 a plurality of G3s may be the same or different to each other. The substituted or unsubstituted methylene group represented by  $(G_3)_a$  is preferably  $-CH_2-$ ,  $-C_2H_4-$ ,  $-C(CH_3)H-CH_2-$ ,  $-C(CH_3)_2-CH_2-$ ,  $-C(CH_3)_2-C(CH_3)H-$ ,  $-C(CH_3)H-C(CH_3)H-$ , or  $-C(CH_3)_2-C(CH_3)_2-$ , R8 is a 25 hydrogen atom,  $G_4$  is -CO- or -SO<sub>2</sub>-, and  $R_9$  is a substituted or unsubstituted alkyl or aryl group having the total carbon atoms of 10 to 70.

Among the compounds represented by the general formula (MC-1), if  $G_1$  is a nitrogen atom,  $G_2$  is a carbon atom, and X is a hydrogen atom, it is preferable that  $R_1$  is a tertiary alkyl group, and  $R_2$  is a group represented by the general formula (BL-1), wherein each of  $R_4$  and  $R_6$  is a group selected from an acylamino group, sulfonamido group, ureido group, alkoxycarbonylamino group, sulfonyl group, carbamoyl group, sulfamoyl group, sulfamoyl group, and alkoxycarbonyl group, each of which is substituted by a substituted or unsubstituted alkyl group having the total carbon atoms of 4 to 70 or by a substituted or unsubstituted aryl group having carbon atoms of 6 to 70.

5

10

15

20

25

Among the compounds represented by the general formula (MC-1), if  $G_1$  is a carbon atom,  $G_2$  is a nitrogen atom, and X is a hydrogen atom, it is preferable that  $R_1$  is a tertiary alkyl group,  $R_2$  is a group represented by the general formula (BL-1) or (BL-2). It is especially preferable that  $R_2$  is a group represented by the general formula (BL-2).

Among the compounds represented by the general formula (MC-1), if  $G_1$  is a nitrogen atom,  $G_2$  is a carbon atom, and X is a split-off group other than a hydrogen atom, it is preferable that  $R_1$  is a tertiary alkyl group,  $R_2$  is a group represented by the general formula (BL-1), at least one of  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$  and  $R_7$ 

is a group selected from an acylamino group, sulfonamido group, ureido group, alkoxycarbonylamino group, sulfonyl group, carbamoyl group, sulfamoyl group, sulfamoylamino group and alkoxycarbonyl group, each of which is substituted by a substituted or unsubstituted alkyl group having the total carbon atoms of 6 to 70 or by a substituted or unsubstituted aryl group having carbon atoms of 6 to 70, and X is a chlorine atom.

5

20

25

Among the compounds represented by the general formula (MC-1), if G<sub>1</sub> is a carton atom, G<sub>2</sub> is a nitrogen atom, and X is a split-off group other than a hydrogen atom, it is preferable that R<sub>1</sub> is a tertiary alkyl group, R<sub>2</sub> is a group represented by the general formula (BL-1) or (BL-2). It is especially preferable that R<sub>2</sub> is a group represented by the general formula (BL-2).

In the present invention, it is preferable that  $G_1$  is a carbon atom and  $G_2$  is a nitrogen atom,  $R_1$  is a tertiary alkyl group,  $R_2$  is represented by the general formula (BL-2), wherein  $G_4$  is  $-SO_2$ -,  $R_9$  is a phenyl group having, as a substituent, at least one group containing an alkyl group of 6- to 50-carbon atoms, and a is 1 or 2. Among these especially preferable is that X is a hydrogen atom or chlorine atom, or substituted phenyloxy group.

Specific compound examples of the general

formula (MC-1) are shown below, but the present invention is not limited to these specific examples.

۲.

ξ.

\$.

1, ,

٤.,

MC-26

۲.

•

$$H_3C$$
 $H_3C$ 
 $H_3C$ 

MC-27

MC-28

ς.

15

The coupler represented by the general

formula (MC-1) of the present invention may be
synthesized by known method. For example, such methods
are described in the specifications of USP's 4,540,654,
4,705,863 and 5,451,501, JP-A's-61-65245, 62-209457,
62-249155, 63-41851, Jpn. Pat. Appln. KOKOKU

Publication No. (hereinafter referred to as "JP-B")
7-122744, JP-B's-5-105682, 7-13309 and 7-82252 or
USP's 3,725,067 and 4,777,121, and JP-A-2-201442,
2-101077, 3-125143 and 4-242249.

Preferable color developing agent for the couplers represented by the general formula (CC-1) or the

ζ.

5

10

15

20

25

general formula (MC-1) to provide a dye having the characteristics defined in the present invention, is N-methyl-N-( $\beta$ -methanesulfonamidoethyl)-3-methyl-4-aminoaniline.

Now, the yellow dye-forming couplers represented by the general formula (YC-1) of the present invention will be described.

In the general formula, R1 represents a substituent other than a hydrogen atom. As the substituent, there can be mentioned, for example, a halogen atom, alkyl group (including cycloalkyl and bicycloalkyl), alkenyl group (including cycloalkenyl and bicycloalkenyl), alkynyl group, aryl group, heterocycle group, cyano group, hydroxyl group, nitro group, carboxyl group, alkoxy group, aryloxy group, silyloxy group, heterocyclic oxy group, acyloxy group, carbamoyloxy group, alkoxycarbonyloxy group, aryloxycarbonyloxy group, amino group (including alkylamino and anilino), acylamino group, aminocarbonylamino group, alkoxycarbonylamino group, aryloxycarbonylamino group, sulfamoylamino group, alkyl- or aryl-sulfonylamino group, mercapto group, alkylthio group, arylthio group, heterocyclic thio group, sulfamoyl group, sulfo group, alkyl- or aryl-sulfinyl group, alkyl- or aryl-sulfonyl group, acyl group, aryloxycarbonyl group, alkoxycarbonyl group, carbamoyl group, aryl- or heterocyclic-azo

ξ.

5

10

15

20

25

group, imido group, phosphino group, phosphinyl group, phosphinyloxy group, phosphinylamino group or silyl group.

These substituents may further have substituents.

As the further substituents, there can be mentioned those set forth above.

Preferably, R1 is a substituted or unsubstituted alkyl group. The total number of carbon atoms had by R1 is preferably in the range of 1 to 60, more preferably 6 to 50, still more preferably 11 to 40, and most preferably 16 to 30. When R1 is a substituted alkyl group, the substituent can be any of those mentioned as R1 substituents above.

R1 is preferably an unsubstituted alkyl group having 11 or more carbon atoms or an alkyl group having its 2-, 3- or 4-position substituted with alkoxy group or aryloxy group. More preferably, R1 is an unsubstituted alkyl group having 16 or more carbon atoms or an alkyl group having its 3-position substituted with an alkoxy group or aryloxy group. Most preferably, R1 is  $C_{16}H_{33}$ ,  $C_{18}H_{37}$ , 3-lauryloxypropyl or 3-(2,4-di-t-amylphenoxy)propyl.

In the general formula (YC-1), Q represents a nonmetallic atomic group capable of forming a 5- to 7-membered ring in cooperation with -N=C-N(R1)-. Preferably, the formed 5- to 7-membered ring is a substituted or unsubstituted single-ring or

.

5

10

15

20

25

condensed-ring heterocycle. More preferably, the ring-constituting atoms are selected from among carbon, nitrogen and sulfur atoms. more preferably, Q is a group represented by the formula  $-C(-R11)=C(-R12)-SO_2-$  or -C(R11)=C(-R12)-CO-. R11 and R12 represent groups capable of bonding with each other to thereby form a 5- to 7-membered ring in cooperation with -C=C-, or each independently represent a hydrogen atom or a substituent. The formed 5- to 7-membered ring is a saturated or unsaturated ring, and may be an alicycle, an aromatic ring or a heterocycle. For example, there can be mentioned a benzene ring, furan ring, thiophene ring, cyclopentane ring or cyclohexane ring. The substituent can be any of those mentioned above as examples of the R1 substituents.

These substituents and rings formed by mutual bonding of multiple substituents may have further substituents (e.g., groups mentioned above as examples of the R1 substituents).

In the general formula (YC-1), R2 represents a substituent other than a hydrogen atom. This substituent can be, for example, any of those mentioned above as examples of the R1 substituents. Preferably, R2 represents a halogen atom (e.g., fluorine atom, chlorine atom or bromine atom), alkyl group (e.g., methyl or isopropyl), aryl group (e.g., phenyl or naphthyl), alkoxy group (e.g., methoxy or

isopropyloxy), aryloxy group (e.g., pheńoxy), acyloxy group (e.g., acetyloxy), amino group (e.g., dimethylamino or morpholino), acylamino group (e.g., acetamido), sulfonamido group (e.g., methanesulfonamido 5 or benzenesulfonamido), alkoxycarbonyl group (e.g., methoxycarbonyl), aryloxycarbonyl group (e.g., phenoxycarbonyl), carbamoyl group (e.g., N-methylcarbamoyl or N, N-diethylcarbamoyl), sulfamoyl group (e.g., N-methylsulfamoyl or N, N-10 diethylsulfamoyl), alkylsulfonyl group (e.g., methanesulfonyl), arylsulfonyl group (e.g., benzenesulfonyl), cyano group, carboxyl group or sulfo group. When the position of R2 is ortho to -CONH-, R2 is more preferably a halogen atom, or alkoxy group, 15 aryloxy group or alkyl group.

In the general formula (YC-1), m is an integer of 0 to 5. When m is 2 or greater, multiple R2s may be the same or different from each other, and may be bonded with each other to thereby form a ring.

20

25

In the general formula (YC-1), X represents a hydrogen atom or a group capable of splitting-off by a coupling reaction with an oxidized product of a developing agent. When X is a group capable of splitting-off by a coupling reaction with an oxidized product of a developing agent, such a group can be, for example, a group that splits off at a nitrogen atom, a group that splits off at an oxygen atom, a group that

splits off at a sulfur atom, or a halogen atom (e.g., chlorine or bromine atom).

The group that splits off at a nitrogen atom can be, for example, a heterocyclic group [preferably 5- to 7-membered, substituted or unsubstituted, saturated or 5 unsaturated, aromatic (herein meaning those having 4n + 2 cyclic conjugated electrons) or nonaromatic, single-ring or condensed-ring heterocyclic group; more preferably a 5- or 6-membered heterocyclic group having its ring forming atoms selected from among carbon, 10 nitrogen and sulfur atoms and having at least one of nitrogen, oxygen and sulfur hetero atoms, such as any of groups from succinimide, maleinimide, phthalimide, diglycolimide, pyrrole, pyrazole, imidazole, 15 1,2,4-triazole, tetrazole, indole, benzopyrazle, benzimidazole, benzotriazole, imidazoline-2,4-dione, oxazolidine-2,4-dione, thiazolidin-2-one, benzimidazolin-2-one, benzoxazolin-2-one, benzothiazolin-2-one, 2-pyrrolin-5-one, 2-imidazolin-5-20 one, indoline-2,3-dione, 2,6-dioxypurine parabanic acid, 1,2,4-triazolidine-3,5-dione, 2-pyridone, 4-pyridone, 2-pyrimidone, 6-pyridazone, 2-pyrazone and 2-amino-1,3,4-thiazolidin-4-one], a carbonamido group (e.g., acetamido or trifluoroacetamido), a sulfonamido 25 group (e.g., methanesulfonamido or benzenesulfonamido), an arylazo group (e.g., phenylazo or naphthylazo) or a carbamoylamino group (e.g., N-methylcarbamoylazo).

Among the groups that splits off at a nitrogen atom, a heterocyclic group is preferred. An aromatic heterocyclic group having one, two, three or four nitrogen atoms as ring-forming atoms, or a heterocyclic group represented by the following general formula (L) is more preferred.

5

10

15

20

25

In the formula, L represents a residue capable of forming a 5- or 6-membered nitrogen-containing heterocycle in cooperation with -NC(=0)-.

Examples thereof are as mentioned above in the description of heterocyclic groups, which are more preferred.

In particular, it is preferred that L represents a residue capable of forming a 5-membered nitrogen-containing heterocycle.

As the group that splits off at an oxygen atom, there can be mentioned, for example, aryloxy group (e.g., phenoxy or 1-naphthoxy), heterocyclic oxy group (e.g., pyridyloxy or pyrazolyloxy), acyloxy group (e.g., acetoxy or benzoyloxy), alkoxy group (e.g., methoxy or dodecyloxy), carbamoyloxy group (e.g., N,N-diethylcarbamoyloxy or morpholinocarbamoyloxy), aryloxycarbonyloxy group (e.g., phenoxycarbonyloxy), alkoxycarbonyloxy group (e.g., methoxycarbonyloxy or

ethoxycarbonyloxy), alkylsulfonyloxy group (e.g., methanesulfonyloxy) or arylsulfonyloxy group (e.g., benzenesulfonyloxy or toluenesulfonyloxy).

٠.

5

10

15

20

25

Among the groups that split off at an oxygen atom, an aryloxy group, acyloxy group and heterocyclic oxy group are preferred.

As the group that splits off at a sulfur atom, there can be mentioned, for example, arylthic group (e.g., phenylthic or naphthylthic), heterocyclic thic group (e.g., tetrazolylthic, 1,3,4-thiadiazolylthic, 1,3,4-oxazolylthic or benzimidazolylthic), alkylthic group (e.g., methylthic, octylthic or hexadecylthic), alkylsulfinyl group (e.g., methanesulfinyl), arylsulfinyl group (e.g., benzenesulfinyl), arylsulfonyl group (e.g., benzenesulfonyl) or alklylsulfonyl group (e.g., methanesulfonyl).

Among the groups that split off at a sulfur atom, arylthio group and heterocyclic thio group are preferred. Heterocyclic thio group is more preferred.

X may have a substituent. The substituent for X can be, for example, any of those mentioned above as examples of the R1 substituents.

Preferably, X represents a group that splits off at a nitrogen atom, a group that splits off at an oxygen atom or a group that splits off at a sulfur atom. More preferably, X represents a group that splits off at a nitrogen atom. Still more preferably,

:

5

10

15

20

X represents any of preferred groups mentioned above with respect to the group that splits off at a nitrogen atom.

Moreover, X may be a photographically useful group. As the photographically useful group, there can be mentioned a development inhibitor, desilvering accelerator, redox compound, dye, coupler or the like, or a precursor thereof.

For the immobilization of the coupler in the photosensitive material, it is preferred that the total number of carbon atoms, including those of substituents, of at least one of Q, R1, X and R2 be in the range of 8 to 50. More preferably, the total number of carbon atoms is in the range of 10 to 40.

Among the couplers of the general formula (YC-1), those of the following general formula (YC-2) are preferred.

In the general formula (YC-2), R1, R2, m and X are as defined above with respect to the general formula (YC-1), and preferred ranges thereof are also as defined there.

In the general formula (YC-2), R3 represents

:..

25

a substituent. This substituent can be, for example, any of those mentioned above as examples of the R1 substituents. Preferably, R3 represents a halogen atom (e.g., fluorine, chlorine or bromine atom), alkyl group 5 (e.g., methyl or isopropyl), aryl group (e.g., phenyl or naphthyl), alkoxy group (e.g., methoxy or isopropyloxy), aryloxy group (e.g., phenoxy), acyloxy (e.g., acetyloxy), amino group (e.g., dimethylamino or morpholino), acylamino group (e.g., acetamido), sulfonamido group (e.g., methanesulfonamido or 10 benzenesulfonamido), alkoxycarbonyl group (e.g., methoxycarbonyl), aryloxycarbonyl group (e.g., phenoxycarbonyl), carbamoyl group (e.g., N-methylcarbamoyl or N, N-diethylcarbamoyl), sulfamoyl 15 group (e.g., N-methylsulfamoyl or N, N-diethylsulfamoyl), alkylsulfonyl group (e.g., methanesulfonyl), arylsulfonyl group (e.g., benzenesulfonyl), cyano group, carboxyl group or sulfo group.

n is an integer of 0 to 4. When n is 2 or greater, multiple R3s may be the same or different from each other, and may be bonded with each other to thereby form a ring.

Among the couplers represented by the general formula (YC-1) or general formula (YC-2) according to the present invention, preferred specific examples will be shown below, which however should not be construed

as limiting the scope of the present invention.

Tautomers resulting from moving of the hydrogen atom at coupling position onto the nitrogen of C=N moiety bonded to the coupling position are also comprehended in the present invention.

5

٠.

.

9.

١.

(2) 
$$C_5H_{11}-t$$
 $C_5H_{11}-t$ 
 $C_6H_{11}-t$ 
 $C_6H_{11}-t$ 
 $C_6H_{11}-t$ 
 $C_6H_{11}-t$ 
 $C_6H_{11}-t$ 

(3) 
$$C_5H_{11}-t$$
 $C_5H_{11}-t$ 
 $C_5H_{11}-t$ 
 $C_5H_{11}-t$ 
 $C_5H_{11}-t$ 
 $C_5H_{11}-t$ 
 $C_5H_{11}-t$ 
 $C_5H_{11}-t$ 

(10) 
$$CC_{16}H_{33}$$
  $CC_{2}NHCOC_{2}H_{5}$ 

٠.

**:** 

•

; ; 3.

. .

÷.

٠.

(29) 
$$C_{18}H_{37}$$
  $C_{2}H_{5}$   $C_{4}H_{8}$   $C_{4}H_{8}$ 

ġ.,

٠.

(31)

O C 18H37

OME

NH

O CO2ME

(33)

O C 18H<sub>37</sub>

N O F

N N O F

N N O F

N O C 18H<sub>37</sub>

N O C 18H<sub>37</sub>

N O C 18H<sub>37</sub>

N O C CO<sub>2</sub>CH<sub>3</sub>

(34) S, O C<sub>18</sub>H<sub>37</sub> OMe

N O OMe

CO<sub>2</sub>CH<sub>3</sub> CI

(35) S, C<sub>18</sub>H<sub>37</sub> OMe NH CO<sub>2</sub>CH<sub>3</sub>

÷.

\*,

· .

3.

The addition amount of dye or dye-providing compound according to the present invention is preferably in the range of 0.01 to 10 g, more preferably 0.1 to 5 g per square meter of image-forming material.

5

10

15

20

25

When the dye-providing compound of the present invention is a coupler, also, the addition amount thereof is preferably in the range of 0.01 to 10 g, more preferably 0.1 to 5 g, and most preferably 0.3 to 2 g, per square meter of silver halide color photosensitive material.

The dye or dye-providing compound according to the present invention can be incorporated in image-forming materials by various known dispersion methods. With respect to a coupler applied to the silver halide color photosensitive material, it is preferred to employ the oil-in-water dispersion method in which the coupler is dissolved in a high-boiling organic solvent (in combination with low-boiling solvent according to necessity), emulsified into an aqueous solution of gelatin and added to a silver halide emulsion.

Examples of the high-boiling solvent used in this oil-in-water dispersion method are described in, e.g., USP 2,322,027. Practical examples of steps, effects, and impregnating latexes of a latex dispersion method as one polymer dispersion method are described in, e.g., USP 4,199,363, West German Patent Application

1

5

(OLS) Nos. 2,541,274 and 2,541,230, JP-B-53-41091, and EP029104, the disclosures of which are herein incorporated by reference. Dispersion using an organic solvent-soluble polymer is described in PCT International Publication W088/00723, the disclosure of which is herein incorporated by reference.

Examples of the high-boiling solvent usable in the abovementioned oil-in-water dispersion method are phthalic esters (e.g., dibutylphthalate, 10 dioctylphthalate, dicyclohexylphthalate, di (2-ethylhexyl) phthalate, decylphthalate, bis(2,4-di-tert-amylphenyl)isophthalate, and bis(1,1-diethylpropyl)phthalate), esters of phosphoric acid and phosphonic acid (e.g., diphenylphosphate, 15 triphenylphosphate, tricresylphosphate, 2-ethylhexyldiphenylphosphate, dioctylbutylphosphate, tricyclohexylphosphate, tri-2-ethylhexylphosphate, tridodecylphosphate, and di(2-ethylhexylphenylphosphate), benzoic esters (e.g., 20 2-ethylhexylbenzoate, 2,4-dichlorobenzoate, dodecylbenzoate, and 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., N, N-diethyldodecaneamide, N, N-diethyllaurylamide, N, N, N, N-tetrakis (2-ethlhexyl) isophthalamide and 25 N, N, N, N-tetrokiscyclohexylisophthalamide), alcohols and phenols (e.g., isostearylalcohol and 2,4-di-tert-amylphenol), aliphatic esters (e.g.,

dibutoxyethyl succinate, bis(2-ethylhexyl) succinate, 2-hexyldecyl tetradecanoate, tributyl citrate, diethyl azelate, isostearyl lactate, and trioctyl tosylate), aniline derivatives (e.g.,

N,N-dibutyl-2-butoxy-5-tert-octylaniline), chlorinated paraffins (paraffins containing 10% to 80% of chlorine), trimesic esters (e.g., tributyl trimesate), dodecylbenzene, diisopropylnaphthalene, phenols (e.g., 2,4-di-tert-amylphenol, 4-dodecyloxyphenol,

4-dodecyloxycarbonylphenol, and
4-(4-dodecyloxyphenylsulfonyl)phenol), carboxylic acids
(e.g., 2-(2,4-di-tert-amylphenoxy butyric acid and
2-ethoxyoctanedecanoic acid), alkylphosphoric acids
(e.g., di-(2-ethylhexyl)phosphoric acid and
diphenylphosphoric acid). In addition to the above
high-boiling solvents, compounds described in, e.g.,

herein by reference.

20

25

Also, an organic solvent having a boiling point of  $30^{\circ}$ C to about  $160^{\circ}$ C (e.g., ethyl acetate, butyl acetate, ethyl propionate, methyl ethyl ketone, cyclohexanone, 2-ethoxyethylacetate, or dimethylformamide) may be used in combination as an auxiliary solvent.

JP-A-6-258803, the disclosure of which is incorporated

The content of coupler of the present invention in the photosensitive material is in the range of 0.01 to 10 g, preferably 0.1 to 2 g per  $m^2$ . Per mol of silver halides contained in the same photosensitive emulsion,

the coupler content is appropriately in the range of  $1 \times 10^{-3}$  to 1 mol, preferably  $2 \times 10^{-3}$  to  $3 \times 10^{-1}$  mol.

When each photosensitive layer has a unit structure consisting of two or more photosensitive emulsion layers of different speeds, it is preferred that the content of coupler of the present invention per mol of silver halides be in the range of  $2 \times 10^{-3}$  to  $2 \times 10^{-1}$  mol in low-speed layers and  $3 \times 10^{-2}$  to  $3 \times 10^{-1}$  mol in high-speed layers.

5

10

15

20

25

The coupler represented by the general formula (CC-1) of the present invention is preferably added to a red-sensitive emulsion layer. The coupler represented by the general formula (MC-1) of the present invention is preferably added to a greensensitive emulsion layer. The coupler represented by the general formula (YC-1) of the present invention is preferably added to a blue-sensitive emulsion layer.

In the present invention, although the use of coupler of the general formula (CC-1), general formula (MC-1) or general formula (YC-1) is preferred, it may be combined with other couplers. However, the higher the degree of contribution of color-forming dye of coupler of the present invention to the total density of dyes forming substantially the same color, the more favorable the obtained results. In particular, the coupler of the present invention is preferably used in such an amount that at least the

degree of contribution to color formation density is 50% or more, more preferably 70% or more.

5

10

15

20

25

In each of the color-forming layers of an imageforming material and a color photosensitive material
for use in duplication, the coupler used in one colorforming layer of an image-forming material and the
coupler used in the corresponding color-forming layer
of a color photosensitive material for use in
duplication does not necessarily the same type. But it
is preferable that, in each of the color-forming
layers, the coupler used in one color-forming layer of
an image-forming material and the coupler used in the
corresponding color-forming layer of a color
photosensitive material for use in duplication are
within the same scope of general formula set forth
above, and it is more preferable that the couplers are
the same type.

Much more preferably, the described cyan coupler, magenta coupler and yellow coupler are each used in both the formation of original images and the formation of duplicate images. More preferably, the cyan coupler and the magenta coupler are simultaneously used in both the formation of original images and the formation of duplicate images.

The magenta coupler represented by the general formula (MC-1) and cyan coupler represented by the general formula (CC-1) according to the present

invention are characterized in that the absorption value of subsidiary absorption maximum wavelength residing in wavelengths quite different from the respective maximum absorption maximum wavelengths of magenta and cyan colors is low. This means that the present invention uses color forming materials of low subsidiary absorption in the original image or duplicate color image-forming material.

5

10

15

20

In particular, the absorption value at the subsidiary absorption maximum wavelength of cyan color-forming dye and/or magenta color-forming dye is preferably 5% or less, more preferably 3% or less, and most preferably 1% or less based on the absorption value at the main absorption maximum wavelength thereof.

The terminology "original image" used herein means images to be duplicated, which refer to, for example, color reversal photosensitive materials, color negative photosensitive materials, thermal paper, pressure sensitive paper, OHP, etc. The preferred form of original image is a color reversal photosensitive material or a color negative photosensitive material. The color reversal photosensitive material is most preferred.

Now, the spectral sensitivity distribution of red-sensitive silver halide emulsion layer according to the present invention will be described.

In the present invention, the spectral sensitivity distribution refers to one obtained by exposing photosensitive materials to radiation of several nanometers (nm) interval spectrum ranging from 400 to 700 nm, defining the exposure amount realizing a given density at each wavelength as the sensitivity at the wavelength and expressing sensitivity values as a function of wavelength.

5

10

15

20

25

In the present invention, appropriate means can be employed for using the spectral sensitivity distribution as a constituent of the invention. For example, the above spectral sensitivity distribution can be obtained by the use of spectral sensitizing dyes. In the present invention, in the regulating of spectral sensitivity distribution by the use of spectral sensitivity distribution by the use of spectral sensitizing dyes, the amount of spectral sensitizing dye is not limited and can be appropriate for realizing desired spectral sensitivity distribution in conformity with the type of dye used and the design of photosensitive material. The type of spectral sensitizing dyes used is not limited.

In the present invention, it is needed for the maximum sensitivity wavelength,  $\lambda$ max (D), of redsensitive silver halide emulsion layer to fall within the range of 630 to 670 nm. Preferably, the maximum sensitivity wavelength falls within the range of 650 to 670 nm.

٠.

5

10

15

In the original images, the silver halide photosensitive materials and silver halide photographic emulsion used therein, to which the method of the present invention may be applied, it is generally possible to use various techniques and inorganic and organic materials described in Research Disclosure Nos. 308119 (1989), and 37038 (1995), the entire contents of which are incorporated herein by reference.

More specifically, techniques and inorganic and organic materials usable in color photosensitive materials to which the method of the present invention can be applied are described in portions of the specification of EP436,938A2 and patents cited below, the entire contents of which are incorporated herein by reference.

		Items	Corresponding portions
20	1)	Layer configurations	page 146, line 34 to page 147, line 25
25	2)	Silver halide emulsions usable together	page 147, line 26 to page 148 line 12
25	3)	Yellow couplers usable together	page 137, line 35 to page 146, line 33, and page 149, lines 21 to 23
30	4)	Magenta couplers usable together	page 149, lines 24 to 28; EP421,453A1, page 3, line 5 to page 25, line 55
35	5)	Cÿan couplers usable together	page 149, lines 29 to 33; EP432,804A2, page 3, line 28 to page 40, line 2
40	6)	Polymer couplers	page 149, lines 34 to 38; EP435,334A2, page 113, line 39 to page 123, line 37

F	7)	Colored couplers	page 53, line 42 to page 137, line 34, and page 149, lines 39 to 45
5	8)	Functional couplers usable together	page 7, line 1 to page 53, line 41, and page 149, line 46 to page 150, line 3; EP435,334A2, page 3, line 1
10			to page 29, line 50
1.5	9)	Antiseptic and mildewproofing agents	page 150, lines 25 to 28
15	10)	Formalin scavengers	page 149, lines 15 to 17
20	11)	Other additives usable together	page 153, lines 38 to 47; EP421,453A1, page 75, line 21 to page 84, line 56, and page 27, line 40 to page 37, line 40
0.5	12)	Dispersion methods	page 150, lines 4 to 24
25	13)	Supports	page 150, lines 32 to 34
30	14)	Film thickness. film physical properties	page 150, lines 35 to 49
	15)	Color development step	page 150, line 50 to page 151, line 47
35	16)	Desilvering step	page 151, line 48 to page 152, line 53
40	17)	Automatic processor	page 152, line 54 to page 153, line 2
40	18)	Washing·stabilizing step	page 153, lines 3 to 37
	Exam	ples	
		The present invention	on will be described
.45	spec	ifically by examples,	but the present invention is
	not	limited to these.	-
	(Exa	mple-1)	

A; Formation of an original sample

Preparation of a silver halide color photosensitive material, Sample A101

Preparation of triacetylcellulose film

• .

20

Triacetylcellulose was dissolved (13 % by weight)

by a common solution casting process in

dichloromethane/methanol = 92/8 (weight ratio), and

triphenyl phosphate and biphenyldiphenyl phosphate in a

weight ratio of 2:1, which are plasticizers, were added

to the resultant solution so that the total amount of

the plasticizers was 14 % to the triacetylcellulose.

Then, a triacetylcellulose film was made by a band

process. The thickness of the support after drying was

205 μm.

Components of undercoat layer

The two surfaces of the triacetylcellulose film were subjected to undercoating treatment. Numbers represent weight contained per liter of an undercoat solution.

The two surfaces of the triacetylcellulose film were subjected to corona discharge treatment before undercoating treatment.

	Gelatin	10.0	g
	Salicylic acid	0.5	g
	Glycerin	4.0	g
25	Acetone	700	mL
	Methanol	200	mL
	Dichloromethane	80	mL

٠.

	Formaldehyde 0.1	mg	
	Water to make 1.0	L	
	Coating of back layers		
	One surface of the undercoated supp	ort was	s coated
5	with the following back layers.		
	1st layer		
	Binder: acid-processed gelatin		
	(isoelectric point: 9.0)	1.00	g
	Polymeric latex: P-2		
10	(average grain size: 0.1 μm)	0.13	g
	Polymeric latex: P-3		
	(average grain size 0.2 μm)	0.23	g
	Ultraviolet absorbent U-1	0.030	g
	Ultraviolet absorbent U-3	0.010	g
15	Ultraviolet absorbent U-4	0.020	g
	High-boiling organic solvent Oil-2	0.030	g
	Surfactant W-3	0.010	g
	Surfactant W-6	3.0	mg
	2nd layer		
20	Binder: acid-processed gelatin		
	(isoelectric point: 9.0)	3.10	g
	Polymeric latex: P-3		
	(average grain size: 0.2 μm)	0.11	g
	Ultraviolet absorbent U-1	0.030	g
25	Ultraviolet absorbent U-3	0.010	g
	Ultraviolet absorbent U-4	0.020	g

High-boiling organic solvent Oil-2 0.030 g

79 Surfactant W-3 0.010 qSurfactant W-6 3.0 mg Dye D-2 0.10 g Dye D-10 0.12 5 Potassium sulfate 0.25 g Calcium chloride 0.5 mg Sodium hydroxide 0.03 q 3rd layer Binder: acid-processed gelatin 10 (isoelectric point: 9.0) 3.30 g Surfactant W-3 0.020 gPotassium sulfate 0.30 0.03 Sodium hydroxide 4th layer 15 Binder: lime-processed gelatin (isoelectric point: 5.4) 1.15 g 1: 9 copolymer of methacrylic acid and methylmethacrylate (average grain size: 2.0 μm) 0.040 q20 6 : 4 copolymer of methacrylic acid and methylmethacrylate (average grain size: 2.0 μm) 0.030 gSurfactant W-3 0.060 g Surfactant W-2 7.0 mg Hardener H-1 25 0.23

Coating of photosensitive emulsion layers

The following photosensitive emulsion layers were

5

. .

coated on the opposite side of the support to the side on which the back layers were coated to make Sample A101. Numbers represent addition amounts per  $m^2$  of the coating surface. Note that the effects of added compounds are not restricted to the described purposes.

1st layer: Antihalation layer

	Black colloidal silver	0.30 g
	Gelatin	2.50 g
	Ultraviolet absorbent U-1	0.10 g
10	Ultraviolet absorbent U-3	0.030 g
	Ultraviolet absorbent U-4	0.050 g
	Ultraviolet absorbent U-5	0.050 g
	Dye D-4	1.0 mg
	Dye D-8	2.5 mg
15	Fine crystal solid dispersion	0.05 g
	of dye E-1	
	2nd layer: Interlayer	
	Gelatin	0.80 g
	Compound Cpd-A	0.2 mg
20	Compound Cpd-G	3.0 mg
	Compound Cpd-H	0.030 g
	Ultraviolet absorbent U-2	0.010 g
	Ultraviolet absorbent U-6	0.020 g
	High-boiling organic solvent Oil-3	0.010 g
25	High-boiling organic solvent Oil-4	0.010 g
	High-boiling organic solvent Oil-7	2.0 mg
	Dye D-7	4.0 mg

:.

3rd layer: Interlayer Yellow colloidal silver 0.020 qGelatin 0.60 High-boiling organic solvent Oil-3 0.010 g High-boiling organic solvent Oil-8 0.010 g 5 4th layer: Low-speed red-sensitive emulsion layer Emulsion A silver 0.15 Emulsion B silver 0.20 Emulsion C silver 0.20 10 Gelatin 0.80 Coupler C-1 0.18 g High-boiling organic solvent Oil-2 0.020 g 5th layer: Medium-speed red-sensitive emulsion layer Emulsion C 0.30 silver q 15 Emulsion D silver 0.20 g Gelatin 0.70 g Coupler C-1 0.20 High-boiling organic solvent Oil-2 0.020 g 6th layer: High-speed red-sensitive emulsion layer 20 Emulsion E 0.25 silver Emulsion F silver 0.30 1.70 g Gelatin 0.70 Coupler C-1 High-boiling organic solvent Oil-2 0.070 g 25 Additive P-1 0.010 g 7th layer: Interlayer Gelatin 0.70

		Additive P-2		0.10	g
		Dye D-5		0.020	g
		Dye D-9		6.0	mg
		Compound Cpd-F		0.010	g
5		Compound Cpd-H		0.040	g
		Compound Cpd-J		3.0	mg
		Compound Cpd-K		5.0	mg
		High-boiling organic solve	ent Oil-6	0.050	g
	8th I	layer: Interlayer			
10		Yellow colloidal silver	silver	0.020	g
		Gelatin		1.00	g
		Additive P-2		0.05	g
		Compound Cpd-A		0.050	g
		Compound Cpd-D		0.030	g
15		Compound Cpd-H		0.050	g
		High-boiling organic solv	ent Oil-3	0.010	g
		High-boiling organic solv	ent Oil-6	0.050	g
	9th I	layer: Low-speed green-sen	sitive emul	lsion 1	layer
		Emulsion G	silver	0.30	g
20		Emulsion H	silver	0.35	g
		Emulsion I	silver	0.30	g
		Gelatin		1.70	g
		Coupler C-2		0.25	g
		High-boiling organic solv	ent Oil-2	0.10	g
25	10th	layer: Medium-speed green	-sensitive	emuls	ion layer
		Emulsion I	silver	0.30	g
		Emulsion J	silver	0.30	g

- 83 -

		Gelatin		0.70	g
		Coupler C-2		0.40	g
		High-boiling organic solv	ent Oil-2	0.16	g
	11th	layer: High-speed green-se	ensitive en	mulsion	layer
5		Emulsion K	silver	0.60	g
		Gelatin		0.80	g
		Coupler C-2		0.50	g
		High-boiling organic solv	ent Oil-2	0.20	g
	12th	layer: Yellow filter laye	r		
10		Yellow colloidal silver	silver	0.010	g
·		Gelatin		1.0	g
		Compound Cpd-C		0.010	g
		Compound Cpd-H		0.10	g
		High-boiling organic solv	ent Oil-1	0.020	g
15		High-boiling organic solv	rent Oil-6	0.10	g
	•	Fine crystal solid disper	sion	0.20	g
		of dye E-2			
	13th	layer: Interlayer			
		Gelatin		0.40	g
20		Compound Cpd-L		0.20	g
		High-boiling organic solv	rent Oil-5	0.010	g
		Dye D-6			mg
	14th	layer: Low-speed blue-sen	sitive emu	lsion :	layer
		Emulsion L	silver	0.10	g
25		Emulsion M	silver	0.20	g
		Emulsion N	silver	0.15	g
		Gelatin		1.30	g

		Coupler C-3		0.35	g
		Compound Cpd-B		0.10	g
		Ultraviolet absorbent U-6		0.010	g
		High-boiling organic solv	ent Oil-2	0.010	g
5	15th	layer: Medium-speed blue-	sensitive e	emulsic	on layer
		Emulsion N	silver	0.15	g
		Emulsion O	silver	0.20	g
		Gelatin		0.80	g
		Coupler C-4		0.25	g
10		Compound Cpd-B		0.10	g
•		Compound Cpd-I		2.0	mg
		High-boiling organic solv	ent Oil-2	0.010	g
	16th	layer: High-speed blue-se	nsitive emu	ulsion	layer
		Emulsion P	silver	0.25	g
15		Emulsion Q	silver	0.25	g
		Gelatin		2.00	g
		Coupler C-4		1.10	g
		High-boiling organic solv	ent Oil-2	0.050	g
		High-boiling organic solv	ent Oil-9	0.050	g
20		Ultraviolet absorbent U-6		0.10	g
		Compound Cpd-I		5.0 r	ng
	17th	layer: 1st protective lay	er		
		Gelatin		1.00	g
		Ultraviolet absorbent U-1		0.15	g
25		Ultraviolet absorbent U-2		0.050	g
		Ultraviolet absorbent U-5		0.20	g
		Compound Cpd-J		5.0	mg

•

- 85 -

		Compound Cpd-A		0.030	g
		Compound Cpd-H		0.20	g
		Dye D-1		8.0	mg
		Dye D-2		0.010	g
5		Dye D-3		0.010	g
		High-boiling organic solve	ent Oil-3	0.10	g
	18th	layer: 2nd protective layer	er		
		Colloidal silver	silver	2.5	mg
		Silver iodobromide emulsion	on grains	(avera	ge grain
10		diameter 0.06 μm, silve	r iodide co	ontent	: 1 mol%)
			silver	0.10	g
		Gelatin		0.80	g
		Ultraviolet absorbent U-1		0.030	g
		Ultraviolet absorbent U-6		0.030	g
15		High-boiling organic solve	ent Oil-3	0.010	g
	19th	layer: 3rd protective layer	er		
		Gelatin		1.00	g
		Polymethylmethacrylate			
		(average grain size 1.5	μm)	0.10	g
20		6: 4 copolymer of methylm	methacryla	te and	
		methacrylic acid (average	ge grain s	ize 1.	5 µm)
				0.15	g
		Silicone oil SO-1		0.20	g
		Surfactant W-1		3.0	mg
25		Surfactant W-2		8.0	mg
		Surfactant W-3		0.040	g
		Surfactant W-7		0.015	g

5

•

In addition to the above compositions, additives F-1 to F-9 were added to all emulsion layers. Also, a gelatin hardener H-1 and surfactants W-3, W-4, W-5, and W-6 for coating and emulsification were added to each layer.

Furthermore, phenol, 1,2-benzisothiazoline-3-one, 2-phenoxyethanol, phenethylalcohol, and p-benzoic butylester were added as antiseptic and mildewproofing agents.

3.

÷.

	ics	(5)		0		0			0						0			
	Other characteristics	(4)	0			_			0								0	
	aract	(3)															0	
	er ch	(2)		0		0			0		•	0			0			
	oth	(1)	0		Ì				0						0			
ple 101	Average	AgI content at grain surface (mo1%)	1.5	2.5		0.5			1.0			1.5			9.0		2.0	
emulsions used in Sample 101		Structure in halide composition of silver halide grains	Double structure	. Triple structure		Quintuple	structure	ا د د د د		stractare	ه [ مربيل حربان	Kadiapro	stractare	ار در انداز	otribite otribite	Sciaccare	Triple structure	
		Av. AgI content (mol%)	5.5	4.5		3.5		-	3.0		ני	?			1.6		3.5	
alide		COV (%)	10	10		19	·		21	-		10			12		ത	Ì
Silver halide		Av. ESD (µm)	0.24	0.25		0.30			0.40			0.50			0.70		0.15	
Table 1 S		Characteristics	Monodisperse tetradecahedral grains	Monodisperse (111) tabular grains	Av. aspect ratio 2.0	Monodisperse (111) tabular grains	Av. aspect ratio 5.0	Monodisperse (111) tabular	grains	Av. aspect ratio 7.0	Monodisperse (111) tabular	grains	Av. aspect ratio 10.0	Monodisperse (111) tabular	grains	Av. aspect ratio 10.5	Monodisperse cubic grains	
		Emulsion	A	В		υ			Д		· · · · · · · · · · · · · · · · · · ·	ĸ			Ŀı		ប	

(Continued)

÷.

				Table 1							
					† ( ) ; ; ; † ( ) ; ; † ( ) ; ; † ( ) ; ; † ( ) ; ; † ( ) ; ; † ( ) ; ; † ( ) ; †	Average	oth	Other characteristics	aract	eristi	cs
		Av.	120	Av. AgI	balide	Agi		-			
Emulsion	Characteristics	ESD	3 9	content	composition	content	()	ć	ć	(	ú
		( <b>m m</b> )	() ()	(mol%)	of silver	at grain	(Ŧ)	(7)	<u>(</u> 2)	( <del>r</del> )	<u> </u>
					halide grains	(mo1%)					
Н	Monodisperse cubic grains	0.20	10	3.0	Triple structure	0.7	0	0		0	
	Monodisperse (111) tabular				⊖ احدن≠ط بدنن						
н	grains	0.35	12	3.5	gtriictbre	4.5		0		-	0
	Av. aspect ratio 4.0				Stractare			·			
	Monodisperse (111) tabular				ار د: ۲۰۰۰ د ارم:						
b	grains	0.50	15	2.5	etulctire etulctire	1.2	0				0
	Av. aspect ratio 10.0				שרדמכרמדה						
	Monodisperse (111) tabular				ال د: د						
X	grains	0.65	13	2.7	בקדוד	1.3	0	0			0
	Av. aspect ratio 10.5				Stractare						
ŀ	Monodisperse	0 31	đ	ر ب	Triple	0 1			C	C	C
7	tetradecahedral grains	10.0		· ·	structure	٥٠,		·	>		
Σ	Monodisperse	35	13	ر د	Quadruple	C	C	C			C
E	tetradecahedral grains	6.0	7	۲.	structure	0.2		>			)
	Monodisperse (111) tabular	٠			واطنطفعنان						
Z	grains	0.33	13	2.1	gtandine	4.0	0	0	0		<del></del>
	Av. aspect ratio 8.0				STRACCATE					_	
	Monodisperse (111) tabular				ָרוני אַנְינייָר. הרונים						
0	grains	0.50	თ	2.5	grantupre	1.0		0			0
	Av. aspect ratio 10.0				פרד מכנתד פ	_		-			
											16.00

(Continued)

٠.

	ics	(5)	0	0		
	erist	(4)				
	aract	(3)				
	Other characteristics	(2)	0			
Table 1	oth	(1)	0	0		
	Average	AgI content at grain (1) (2) (3) (4) (5) surface (mol%)	0.5	0.3		
	(%::40::24:0	structure in halide composition of silver halide grains	Triple structure	Quadruple structure		
		Av. AgI content (mol%)	1.8	8.0		
		COV (%)	21	15		
		Av. ESD (µm)	0.75	06.0		
		Characteristics	Monodisperse (111) tabular grains Av. aspect ratio 12.0	Monodisperse (111) tabular grains Av. aspect ratio 12.0		
		Emulsion	Ω	ø		

Av. ESD = Equivalent-sphere average grain size; COV = Coefficient of variation

(Other characteristics)

The mark "O" means each of the conditions set forth below is satisfied.

- A reduction sensitizer was added during grain formation;
  - (2) A selenium sensitizer was used as an after-ripening agent
    - (3) A rhodium salt was added during grain formation.
- (4) A shell was provided subsequent to after-ripening by using silver nitrate in an amount of 10%, together with the equimolar amount in terms of silver molar ratio, of the emulsion grains at that time, of potassium bromide
  - grain was observed by (5) The presence of dislocation lines in an average number of ten or more per a transmission electron microscope.

Note that all the lightsensitive emulsions were after-ripped by the use of sodium thiosulfate, sodium thiocyanate, and sodium aurichloride. Note, also, a iridium salt was added during grain formation. Note, also, that chemically-modified gelatin whose amino groups were partially converted to phthalic E, H, J, N, and Q. ΰ acid amide, was added to emulsions B, .

÷.

	Table 2 S	Spectral sensitization of	of Emulsions A to Q
מייים ביניים	Spectral sensitizing	izing Addition amount per mol	0:2 0:4 to 2000 04+ to 14: 4: 50: 4: E
FINALSTON	dye added	of silver halide (g)	ilming ar which the sensitizing aye was added
	S-1	0.01	Subsequent to after-ripening
	S-2	0.20	Prior to after-ripening
A	S-3	0.02	Prior to after-ripening
	8-8	0.25	Prior to after-ripening
	S-14	0.01	Prior to after-ripening
	S-2	0.20	Prior to after-ripening
ρ	S-3	0.02	Prior to after-ripening
Q —	S−8.	0.20	Prior to after-ripening
	S-14	0.01	Prior to after-ripening
	S-2	0.25	Prior to after-ripening
	S-3	0.04	Prior to after-ripening
υ	8-8	0.25	Prior to after-ripening
	S-13	0.02	Subsequent to after-ripening
	S-14	0.04	Subsequent to after-ripening
	S-2	0.25	Prior to after-ripening
	8-3	0.03	. Prior to after-ripening
ם	8-8	0.25	Prior to after-ripening
	S-13	0.01	Prior to after-ripening
	S-1	0.01	Subsequent to after-ripening
	S-2	0.20	Prior to after-ripening
Ĺ	S-3	0.05	Prior to after-ripening
1	8-8	0.25	Prior to after-ripening
	S-13	0.01	Prior to after-ripening
	S-14	0.02	Prior to after-ripening

(Continued)

•.

		Table 2	
Emulsion		Addition amount per mol of	izing Addition amount permol of Timing at which the sensitizing dve was added
	dye added	silver halide (g)	
	S-2	0.20	Prior to after-ripening
Ĺ.	8–3	0.04	Prior to after-ripening
ч	8-8	0.20	Prior to after-ripening
	S-14	0.02	Prior to after-ripening
	S-4	0.3	Subsequent to after-ripening
ტ	S-5	0.05	Subsequent to after-ripening
	S-12	0.1	Subsequent to after-ripening
	S-4	0.2	Prior to after-ripening
н	8-9	0.15	Prior to after-ripening
	S-14	0.02	Prior to after-ripening
	S-4	0.3	Prior to after-ripening
н	8-9	0.2	Prior to after-ripening
	S-12	0.1	Prior to after-ripening
	S-4	0.35	Prior to after-ripening
þ	S-5	0.05	Subsequent to after-ripening
	s-12	0.1	Prior to after-ripening
	S-4	0.3	Prior to after-ripening
×	8-9	0.05	Prior to after-ripening
<b>4</b>	S-12	0.1	Prior to after-ripening
	S-14	0.02	Prior to after-ripening

(Continued)

92

0
ø
Ē
ď
Ë

·

÷.

		7 ATONI	
R.m.1 sion	12	Addition amount permol of	ing Addition amount per mol of miming at which the sensitizing dye was added
TOTOTOM	dye added	silver halide (g)	י דווודוון מר יוודנון כנוים בכוודנדים אלה יומד מממכים
	9-S	0.1	Subsequent to after-ripening
L, M	S-10	0.2	Subsequent to after-ripening
	S-11	0.05	Subsequent to after-ripening
	9-S	0.05	Subsequent to after-ripening
2	S-7	0.05	Subsequent to after-ripening
<b>Z</b>	S-10	0.25	Subsequent to after-ripening
	S-11	0.05	Subsequent to after-ripening
C	S-10	0.4	Subsequent to after-ripening
)	S-11	0.15	Subsequent to after-ripening
	S-6	0.05	Subsequent to after-ripening
ርብ	S-10	0.3	Prior to after-ripening
	S-11	0.1	Prior to after-ripening
	9-S	0.05	Prior to after-ripening
C	S-7	0.05	Prior to after-ripening
×	S-10	0.2	Prior to after-ripening
	S-11	0.25	Prior to after-ripening

C-1 
$$\begin{array}{c} OH \\ C_{12}H_{25} \\ O-CHCONH \end{array}$$
 NHCOC $_3F_7$ 

\* \*

Oil-1 Tri (n-hexyl) phosphate

Oil-2 Tricresyl phosphate

Oil-3  $O=P - \left( \begin{array}{ccc} CH_3 & CH_3 \\ CH_2CH_2CHCH_2CCH_3 \\ CH_3 \end{array} \right)_3$ 

Oil-4 Tricyclohexyl phosphate

Oil-5 Bis (2-ethylhexyl) succinate

Oil-6 CON-(CH<sub>2</sub>CHC<sub>4</sub>H<sub>9</sub>)<sub>2</sub>
C<sub>2</sub>H<sub>5</sub>
CON-(CH<sub>2</sub>CHC<sub>4</sub>H<sub>9</sub>)<sub>2</sub>
C<sub>2</sub>H<sub>5</sub>

Oil-7  $HO \longrightarrow C_5H_{11}(t)$   $C_5H_{11}(t)$ 

Oil-8  $C_{11}H_{23}CON < C_{2}H_{5}$ 

Oil-9  $C_4H_9$   $C_4H_9$   $OC_4H_9$   $OC_4H_9$ 

$$C_8H_{17}$$
OH
 $C_8H_{17}$ 
OH

### Cpd-B

## Cpd-C

5

3.

\*\* •

# Cpd-D

Cpd-E

(n)
$$C_{15}H_{31}CONH$$
OH
$$CH_2CONH$$

$$C_3H_7$$

## Cpd-H

OH 
$$C_{6}H_{13}(n)$$
  $C_{8}H_{17}(n)$ 

5

# Cpd-J

Cpd-K

Cpd-L

U-1

$$\bigcap_{N} \bigcap_{N} \bigcap_{C_4H_9(sec)} C_4H_9(sec)$$

U-2

$$CH_3$$
  $CH=C$   $COOC_{16}H_{33}$ 

U-3

$$CI \longrightarrow N \longrightarrow OH \\ C_4H_9(t)$$

$$(t)C_4H_9$$

U-4

$$\bigcap_{N} \bigvee_{N} \bigcap_{(t)C_4H_9}^{OH}$$

U-5

$$(C_2H_5)_2$$
NCH=CH-CH=C  $SO_2$ 

U-6

CI OH 
$$C_4H_9(t)$$
  $(CH_2)_2COOC_8H_{17}$ 

S-1

**::** .

S-2

$$\begin{array}{c|c} & C_2H_5 \\ & &$$

S-3

$$C_4H_9-N \qquad N-CH_2CH_2OCH_3$$

$$O \qquad O \qquad O$$

$$S \qquad CH-C-CH$$

$$O \qquad O \qquad S$$

$$C_2H_5 \qquad CH_3$$

S-4

$$\begin{array}{c|c} C_2H_5 \\ C_1 & C_1 \\ C_1 & C_2H_5 \\ C_1 & C_2H_5 \\ C_2H_5 & C_2H_5 \\ C_2$$

S-5

..

∵.

S-6

S-7

$$\begin{array}{c|c} CH & S \\ & & \\ & & \\ & (CH_2)_4SO_3H \cdot N(C_2H_5)_3 \\ & & (CH_2)_3SO_3^{\Theta} \end{array}$$

S-8

:.

٠.

S-10

O

CH

N

(CH<sub>2</sub>)<sub>3</sub>

SO<sub>3</sub>H·N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>

(CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>
$$\Theta$$

S-11 S 
$$CH \longrightarrow N$$
  $CH \longrightarrow N$   $(CH_2)_2$   $(CH_2)_2$   $(CH_2)_2$   $(CH_2)_2$   $(CH_2)_2$   $(CH_2)_3$   $(CH_2)$ 

S-12 O CH=C-CH= 
$$\stackrel{\circ}{\bigcirc}$$
 CH=C-CH=  $\stackrel{\circ}{\bigcirc}$  CH<sub>2</sub>COOH

S-13

\*\* .

S-14

:.

: .

D-1 
$$C_2H_5O$$
  $CH-CH=CH-CH=CH$   $OC_2H_5$   $OC_2H_5$ 

$$SO_3K$$
  $SO_3K$ 

D-4 CONH(CH<sub>2</sub>)<sub>3</sub>O C<sub>5</sub>H<sub>11</sub>(t) 
$$C_5H_{11}(t)$$
  $C_5H_{11}(t)$   $C_5H_{11}(t)$ 

\*\* •

D-6 D-7 
$$C_2H_5$$
HO CH-CH=CH OH OH C $_2H_5$ 
SO $_3$ Na SO $_3$ Na  $C_2H_5$ 

D-8 OH CONHC<sub>12</sub>H<sub>25</sub> OH NHCOCH<sub>3</sub> OCH<sub>2</sub>CH<sub>2</sub>O 
$$\longrightarrow$$
 N=N  $\longrightarrow$  SO<sub>3</sub>Na SO<sub>3</sub>Na

D-9 
$$H_5C_2OOC \nearrow CH-CH=CH-CH=CH$$

$$\downarrow N$$

$$\downarrow$$

.

÷.

HOOC — CH3 CH-CH=CH— NN N COOH

CH<sub>3</sub> COOCH<sub>3</sub> COOCH<sub>3</sub>

 ••

\*.

٠.

Preparation of organic solid dispersed dye (Preparation of fine crystalline solid dispersion of dye E-1)

5

10

15

20

25

100 g of Pluronic F88 (an ethylene oxide-propylene oxide block copolymer) manufactured by BASF CORP. and water were added to a wet cake of the dye E-1 (the net weight of E-1 was 270 g), and the resultant material was stirred to make 4,000 g. Next, the Ultra Visco Mill (UVM-2) manufactured by Imex K.K. was filled with 1,700 mL of zirconia beads with an average grain size of 0.5 mm, and the slurry was milled through this UVM-2 at a peripheral speed of approximately 10 m/sec and a discharge rate of 0.5 L/min for 2 hr. The beads were filtered out, and water was added to dilute the material to a dye concentration of 3%. After that, the material was heated to 90°C for 10 hr for The average grain size of the stabilization. obtained fine dye grains was 0.30 µm, and the grain size distribution (grain size standard deviation  $\times$  100/average grain size) was 20%.

(Preparation of fine crystalline solid dispersion of dye E-2)

Water and 270 g of W-4 were added to 1,400 g of a wet cake of E-2 containing 30 weight% of water, and the resultant material was stirred to form a slurry having an E-2 concentration of 40 weight%. Next, the Ultra Visco Mill (UVM-2) manufactured by Imex K.K. was

filled with 1,700 mL of zirconia beads with an average grain size of 0.5 mm, and the slurry was milled through this UVM-2 at a peripheral speed of approximately 10 m/sec and a discharge rate of 0.5 L/min for 8 hr, thereby obtaining a solid fine-grain dispersion of E-2. This dispersion was diluted to 20 weight% by ion exchange water to obtain a fine crystalline solid dispersion. The average grain size was 0.15 µm.

5

10

15

20

25

Subsequently, sample A102 was prepared by replacing the couplers and high-boiling organic solvents of the 4th, 5th and 6th layers of the sample A101 as indicated in Table 3. The replacement of couplers was conducted so that the same cyan maximum density was realized upon processing through the following Development Processing A. Further, the coupler replacement was conducted so that in the layers of identical color sensitivity the coupler ratios among high-speed, medium-speed and low-speed layers were the same as in the sample A101. With respect to high-boiling organic solvents, the replacement thereof was conducted as indicated in Table 3, and expressed in terms of mass weight ratio to coupler. The amount of Ag was changed as indicated in Table 3. Further additives other than those specifically mentioned were not changed from those of the sample A101.

က
ø
بَ
g
Ë

**"**.

ler in 4th, High-boiling organic solvent and 6th (Wt. ratio with respect to coupler)	C-1 oil-2 (0.1)	cc-2 cc-2 coil-B (0.20)  Reduced to 0.7 times with respect to sample A101 in each of the layers
Coupler in 4th, 5th and 6th layers	C-1	cc-2
Sample	A101	A102

oil-B

5

**;** .

In this Example, the following Development

Processing A was carried out. In the processing, each solution was used after samples A101 and A102, 60% of which were subjected to complete exposure to white light, were applied at a ratio of 1:1 until the replenishing volume became 5 times the tank capacity.

10	Step	Time (min)	Temp. $(^{\circ}\!$	Tank vol.	Replenish- ment rate (mL/m <sup>2</sup> )
	1st Develop- ment	6	38	195	. 2200
15	1st Aater washing	2	38	55	4000
	Reversal	2	38	90	1100
20	Color develop- ment	6	38	180	1500
	Prebleaching	2	38	70	1100
25	Bleaching	6	38	160	220
	Fixing	4	38	120	1100
30	2nd Water washi	ng 4	38	100	4000
30	Final rinse	1	25	45	1100

The composition of each processing solution was as follows.

35	~		
	(1st development solution)	Tank solution	Replenisher
40	Pentasodium nitrilo-N,N,N-t	rimethylene	ephosphonate 1.5g
	Pentasodium diethylenetriam	inepentace	tate 2.0g

\*.

	Sodium sulfite	30g	30g
	Hydroquinone/potassium monos	ulfonate 20g	20g
5	Potassium carbonate	15g	20g
	Sodium bicarbonate	12g	15g
10	1-Phenyl-4-methyl-4-hydroxym	nethyl-3-pyrazol 1.5g	idone 2.0g
	Potassium bromide	2.5g	1.4g
15	Potassium thiocyanate	1.2g	1.2g
	Potassium iodide	2.0 mg	-
20	Diethylene glycol	13g	15g <sub>.</sub>
20	Water to make	1000 mL	1000 mL
	рН	9.60	9.60
25	This pH was adjusted by t	he use of sulfu	ric acid
0:	r potassium hydroxide.		
30	reversal solution)	Tank Repl	enisher
30	Pentasodium nitrilo-N,N,N-tr	3.0g same	phonate as the solution
35	Stannous chloride dihydrate	1.0g	
	p-Aminophenol	0.1g	
40	Sodium hydroxide	8g	
40	Glacial acetic acid	15 mL	
	Water to make	1000 mL	
45	Hq	6.00	

This pH was adjusted by the use of acetic acid or sodium hydroxide.

\*\*.

	(Color developer)	Tank solution	Replenisher
5	Pentasodium nitrilo-N,N,N-t	rimethylene 2.0g	ephosphonate 2.0g
	Sodium sulfite	7.0g	7.0g
10	Trisodium phosphate dodecah	ydrate 36g	36g
	Potassium bromide	1.0g	-
15	Potassium iodide	90 mg	-
13	Sodium hydroxide	3.0g	3.0g
	Citrazinic acid	1.5g	1.5g
20	N-Ethyl-N-( $\beta$ -methanesulfon aminoaniline 3/2 sulfate mo		-3-methyl-4-
	3,6-Dithiaoctane-1,8-diol	1.0g	1.0g
25	Water to make	1.0g 1000 mL	1000mL
	pH	11.80	12.00
	рп	11.00	12.00
30	This pH was adjusted by	the use of	sulfuric acid
	or potassium hydroxide.		
35	(Prebleaching)	Tank solution	Replenisher
33	Disodium ethylenediaminetet	raacetate 0 8.0g	dihydrate 8.0g
40	Sodium sulfite	6.0g	8.0g
40	1-Thioglycerol	0.4g	0.4g
45	Formaldehyde/sodium bisulfi	te adduct 30g	35g
45	Water to make	1000 mL	1000mL
	Н	6.50	6.50
50	This pH was adjusted by	the use of	acetic acid or
	sodium hydroxide.		

	(Bleaching solution)	Tank solution	Replenisher
5	Disodium ethylenediaminetet	raacetate o 2.0g	dihydrate 4.0g
10	Fe(III) ammonium ethylenedi dihydrate	aminetetraa 120g	acetate 240g
10	Potassium bromide	100g	200g
	Ammonium nitrate	10g	20g
15	Water to make	1000 mL	1000mL
	На	5.70	5.50
	This pH was adjusted by	the use of	nitric acid or
20	sodium hydroxide.		
	(Fixing solution)	Tank solution	Replenisher
25	Ammonium thiosulfate	80g	same as the tank solution
	Sodium sulfite	5.0g	
30	Sodium bisulfite	5.0g	
	Water to make	1000 mL	
35	рН	6.60	
	This pH was adjusted by	the use of	acetic acid or
	aqueous ammonia.		
40	(Stabilizer)	Tank solution	Replenisher
	1,2-Benzoisothiazolin-3-one	e 0.02g	0.03g
45	Polyoxyethylene p-monononyl (av. deg. of polymn. 10)	phenyl eth 0.3g	er 0.3g
	Polymaleic acid (av. mol.wt	2,000) 0.1g	0.15g
50	Water to make	1000 mL	1000mL

рН 7.0 7.0

In the above development processing operation, continuous solution circulation and agitation was conducted in each of the baths. In each tank, a burst pipe provided with small holes of 0.3 mm diameter at intervals of 1 cm was arranged on the bottom thereof so as to effect continuous bursting of nitrogen gas and agitation. The bursting agitation was not performed in the pre-bleaching bath and the second washing bath.

B; Procedure for preparing photosensitive material for duplication

The following silver halide color photosensitive material for duplication, sample B101, was prepared.

A support of 195  $\mu m$  thick undercoated triacetylcellulose film was coated with the silver halide emulsions of Tables 4 and 5, so that a multilayer color photosensitive material having layers of the following compositions, sample B101, was obtained. The figures are for the addition amount per  $m^2$ . The effects of added compounds are not limited to described uses.

1st layer: Antihalation layer

5

15

20

	Black colloidal silver	silver	0.28	g
	Gelatin		2.25	g
25	Ultraviolet absorber Ul-	1	0.05	g
	Ultraviolet absorber U1-2	2	0.02	g
	Ultraviolet absorber U1-	3	0.04	g

**\$**\* .

High-boiling organic solvent Oil1-1 0.03 g High-boiling organic solvent Oil1-3 0.08 g Fine crystalline solid dispersion of dye E1-1 0.05 g5 2nd layer: Interlayer 0.39 g Gelatin Compound Cpd1-A 1.1 mg High-boiling organic solvent Oil1-2 0.02 g Dye D1-1 9.0 mg 3rd layer: Interlayer 10 Silver iodobromide emulsion grains having grain surface fogged (av. grain diam. 0.06  $\mu m$  and silver iodide content 1 mol%) silver 0.03 gGelatin 0.45 g15 4th layer: Low-speed red-sensitive emulsion layer Emulsion A1 silver 0.33 g0.68 g Gelatin 0.06 qCoupler Cp-1 0.15 qCoupler Cp-2 5.0 mg20 Compound Cpd1-B 1.0 mg Compound Cpd1-C 0.01 qCompound Cpd1-D High-boiling organic solvent Oil1-3 0.05 g 5th layer: Medium-speed red-sensitive emulsion layer 25 Emulsion B1 silver 0.34 gEmulsion C1 silver 0.09 g 1.46 g Gelatin

Coupler Cp-1 0.30 gCoupler Cp-2 0.30 gCompound Cpd1-C 2.0 mg High-boiling organic solvent Oil1-3 0.10 g 6th layer: High-speed red-sensitive emulsion layer 5 Emulsion D1 0.37 g silver Emulsion E1 silver 0.21 qGelatin 1.45 g Coupler Cp-1 0.18 g10 Coupler Cp-2 0.40 gCoupler Cp-3 0.02 g3.0 mg Compound Cpd1-D High-boiling organic solvent Oil1-3 0.13 g 7th layer: Interlayer 15 Gelatin 0.40 gColor mixing preventive Cpd1-E 0.02 gHigh-boiling organic solvent Oil1-1 0.02 g Solid dispersion of dye E1-2 0.01 g 8th layer: Interlayer 20 Yellow colloidal silver silver 0.04 g1.20 g Gelatin  $0.15 \, q$ Compound Cpd1-C High-boiling organic solvent Oil1-2 0.46 g Solid dispersion of dye E1-1 0.10 g25 Additive M1-1 0.05 g9th layer: Low-speed green-sensitive emulsion layer Emulsion F1 0.40 gsilver

**:**.

\$t.,

		Silver iodobromide emulsi	on grains l	naving surface
		and internal portion for	gged	
		(av. grain diam. 0.1 μm	and silve	r iodide
		content 1 mol%)	silver	0.04 g
5		Gelatin		1.60 g
		Coupler Cp-4		0.02 g
		Coupler Cp-5		0.10 g
		Coupler Cp-6		0.02 g
		Coupler Cp-7		0.15 g
10		Compound Cpd1-C		0.9 mg
		Compound Cpd1-F		9.0 mg
		High-boiling organic solve	ent Oil1-3	0.23 g
	10th	layer: Medium-speed green	-sensitive	emulsion layer
		Emulsion G1	silver	0.37 g
15		Emulsion H1	silver	0.12 g
		Gelatin		0.93 g
		Coupler Cp-4		0.25 g
		Coupler Cp-5		0.02 g
		Coupler Cp-7		0.02 g
20		Compound Cpdl-C		0.6 mg
		Compound Cpd1-F		7.0 mg
		High-boiling organic solv	ent Oil1-3	0.12 g
	11th	layer: High-speed green-se	ensitive er	mulsion layer
		Emulsion I1	silver	0.37 g
25		Emulsion J1	silver	0.28 g
		Gelatin		1.74 g
		Coupler Cp-4		0.40 g

Coupler Cp-5 0.02 qCoupler Cp-7 0.02 gCompound Cpd1-C 1.3 mg Compound Cpd1-F 0.02 g5 High-boiling organic solvent 0il1-3 0.26 g 12th layer: Interlayer Gelatin 0.39 gCompound Cpd1-C 0.02 gFormalin scavenger Cpd1-G 1.20 g 10 Formalin scavenger Cpd1-H 0.38 gHigh-boiling organic solvent Oil1-2 0.09 g Additive M1-1 0.11 g13th layer: Yellow filter layer Yellow colloidal silver silver 0.19 g15 Gelatin 0.05 gColor mixing preventive Cpd1-E 0.05 gColor mixing preventive Cpd1-I 0.01 qHigh-boiling organic solvent Oil1-2 0.02 g Fine crystalline solid dispersion of dye E1-3 20 0.05 qAdditive M1-1 0.63 q14th layer: Interlayer Silver iodobromide emulsion grains (av. grain diam. 0.06  $\mu$ m and silver iodide content 1 mol%) 25 silver 0.10 qGelatin 0.33 gColor mixing preventive Cpd1-E 0.03 g

	15th	layer: Low-speed blue-sens	sitive emul	sion	layer
		Emulsion K1	silver	0.25	g
		Emulsion L1	silver	0.12	g
		Emulsion M1	silver	0.12	g
5		Gelatin		1.57	g
		Coupler Cp-8		0.63	g
	16th	layer: High-speed blue-ser	nsitive emu	lsior	ı layer
		Emulsion M1	silver	0.10	g
		Emulsion N1	silver	0.13	g
10		Emulsion O1	silver	0.30	g
		Gelatin		1.92	g
		Coupler Cp-8		1.00	g
		Coupler Cp-9		0.10	g
		Coupler Cp-10		0.10	g
15	17th	layer: 1st protective lay	er		
		Gelatin		1.37	g
	•	Ultraviolet absorber U1-1		0.02	g
		Ultraviolet absorber U1-4		0.01	g
		Ultraviolet absorber U1-5		0.04	g
20		Dye D1-2		0.01	g
		Dye D1-3		0.02	g
		Dye D1-4		5.0 r	ng
		Dye D1-5		5.0 r	ng
		Dye D1-6		0.02	g
25	18th	layer: 2nd protective lay	er		
		Colloidal silver	silver	0.1 r	ng
		Silver iodobromide emulsi	on grains	(av. 9	grain

15

20

25

diam.	0.06	μm	and	silver	iodide	content	1	mol%)	
-------	------	----	-----	--------	--------	---------	---	-------	--

		diam.	0.06	μm a	nd	silve	r iodide	content 1	mol%)
							silver	0.10 g	
		Gelatin						0.66 g	
	19th	layer: 3	Brd pr	otec	tiv	e laye	er		
5		Gelatin						1.39 g	
		Polymeth	hyl me	ethac	ryl	ate			
			(av. ]	parti	cle	diam	. 1.5 µm	) 8.0 mg	
		Methyl r	methad	cryla	ite/	metha	crylate	6:4 copoly	mer
		(av. p	partio	cle d	liam	. 1.5	μm)	0.23 g	
10		Silicon	e oil					0.03 g	
		Surfacta	ant W1	L-1				3.0 mg	

Surfactant W1-2

In addition to the above components, additives F1-1 to F1-11 were added to all the above emulsion layers. In the sample B101, the compound F1-6 was added to the 19th layer in an amount of 0.3 mmol per mol of photosensitive silver halides.

6.0 mg

Furthermore, in addition to the above components, gelatin hardener H1-1 and surfactants for coating and emulsification W1-3 to W1-7 were added to the above layers.

Still further, phenol, 1,2-benzisothiazolin-3-one, 2-phenoxyethanol, phenethyl alcohol and butyl pbenzoate were added as antiseptics and mildewproofing agents.

The opposite side of the support was furnished with the following back layers.

e.

	B-1 layer: Back layer	
	Acid-treated gelatin	2.0 g
	Ultraviolet absorber U1-1	0.1 g
	Ultraviolet absorber U1-2	0.05 g
5	Ultraviolet absorber U1-3	0.03 g
	High-boiling organic solvent Oill-1	0.1 g
	Additive M1-1	0.6 g
	Additive M1-2	0.7 g
	B-2 layer: Back 1st protective layer	•
10	Acid-treated gelatin	9.0 g
	B-3 layer: Back 2nd protective layer	
	Alkali-treated gelatin	1.5 g
	Polymethyl methacrylate	
	(av. particle diam. 1.5 $\mu$ m)	0.02 g
15	Methyl methacrylate/methacrylate 6:4	1 copolymer
	(av. particle diam. 1.5 $\mu$ m)	0.05 g
	Strontium/barium sulfate grains	
	(av. grain diam. 1.4 $\mu$ m)	0.15 g
•	Surfactant W1-2	5 mg
20	Surfactant W1-3	50 mg
	Further, in addition to the above co	omponents,
	sodium chloride, potassium nitrate, calci	um chloride,
	surfactant for coating W1-6, surfactant f	for
	emulsification W1-4 and gelatin hardener	H1-1 were
25	added to the layers of sample B101. Stil	l further,
	phenol, 1,2-benzisothiazolin-3-one, 2-phe	enoxyethanol,
	phenyl isothiocyanate and phenethyl alcoh	nol as

..

₹.,

antiseptics and mildewproofing agents were added to the layers of sample B101.

C p - 1

$$C_{\mathfrak{g}}H_{\mathfrak{g}}$$

:.

**!** 

C p - 2

$$C_2H_5$$

$$C_3H_5$$

$$C_3H_{11} - O - CHCONH$$

$$C_3H_{11} + O - CHCONH$$

C p - 4   
-(CH<sub>2</sub> - CH 
$$\frac{1}{750}$$
 (CH<sub>2</sub> - CH  $\frac{1}{750}$  COOC<sub>4</sub>H<sub>8</sub> COOC<sub>4</sub>H<sub>8</sub> The numbers represent wt. % Average mol. wt.: about 25,000

· .

$$C p - 5$$

$$(t) C_5 H_{11} \longrightarrow 0 CH_2 CONH \longrightarrow CONH$$

$$C1 \longrightarrow C1$$

$$C1 \longrightarrow C1$$

$$C_{2}H_{5} \longrightarrow C_{2}H_{4}$$

$$OC_{18}H_{37} \longrightarrow NH$$

$$SO_{2}NH - CH_{3}$$

$$C_{2}H_{5} \longrightarrow C_{2}NH$$

$$\begin{array}{c|c} C & C_2 H_5 \\ \hline \\ (t) C_5 H_{11} & OCHCONH \\ \hline \\ (t) C_5 H_{11} & CONH \\ \hline \\ C1 & C1 \\ \hline \end{array}$$

÷.

O i I I - I Dibutyl phthalate

O i 11-2 (iso-C<sub>8</sub>H<sub>18</sub>)<sub>8</sub> P=0

O i 11-3 Tricresyl phosphate

Cpd1-A

Cpdl-B

Cpd1-C

410

C p d 1 - D

C p d 1 - E

C p d 1 - F

C p d 1 - G

٠,

C p d 1 - H

$$0 = \bigvee_{N = 1}^{H} \bigvee_{N = 0}^{CH_s} 0$$

Cpdl-I

## U 1 – 2

### U 1 - 3

### U1-4

$$CH_{3} \longrightarrow CH = C < \frac{CN}{C00C_{16}H_{35}}$$

## U 1 – 5

$$(C_2H_5)_2NCH = CH - CH = C < \frac{COOC_8H_{17}}{SO_2}$$

4° 6

$$D1 - 1$$

**4°** &

### D1 - 2

### D1 - 3

# D1-4

D1 = 5

÷.

**.** .

D 1 - 6

E 1-1

E1 - 2

.

٠,٠

E1-3

H1 - 1

$$\begin{aligned} \text{CH}_2 &= \text{CH} - \text{SO}_2 - \text{CH}_2 - \text{CONH} - \text{CH}_2 \\ &\mid \\ \text{CH}_2 &= \text{CH} - \text{SO}_2 - \text{CH}_2 - \text{CONH} - \text{CH}_2 \end{aligned}$$

W1-1

 $C_8P_1$ ,  $SO_2NHCH_2CH_2CH_2OCH_2CH_2N(CH_3)$ ,

W1-2

W1 - 3

$$\begin{array}{c} CH_2\,COOCH_2\,CH(C_2H_5)\,C_4H_8\\ \\ |\\ NaO_3\,S-CHCOOCH_2\,CH(C_2H_5)\,C_4H_9 \end{array}$$

W1 - 4

$$F_1 - 3$$

٠,٠

$$F1-4$$

$$F1-6$$

$$F1 - 7$$

$$\text{OSH} \text{-} \text{SH}$$

$$F_1 - 9$$

$$F1-10$$

$$F_1 - 11$$

4
Ψ
것
ap
ĕ

Emulsion	Characteristics of grains	Equivalent sphere average grain diameter(µm)	Coefficient of variation (%)	Silver iodide content(%)
A1	Surface low-iodide triple structure monodisperse cubic grains	0.12	8	4.5
B1	Surface low-iodide triple structure monodisperse cubic grains	0.14	12	4.5
C1	Quadruple structure cubic grains	0.28	15	4.5
D1	Quadruple structure cubic grains	0.35	15	4.5
E1	Polydisperse twin crystal grains	1.15	28	3.0
F1	e low-iodide sperse cubic	0.32	12	2.0
61	Surface low-iodide triple structure cubic grains into which Rh salt is	0.35	16	4.7
	doped			
H1	Quadruple structure cubic grains	0.43	12	4.7
11	Monodisperse tabular grains Aspect ratio 6.0	0.56	14	4.0
11	Monodisperse tabular grains Aspect ratio 9.0	1.20	18	3.0
K1	Surface low-iodide triple structure cubic grains into which Rh salt is doped	0.25	&	2.2
L1	Surface low-iodide triple structure cubic grains	0.22	12	2.2
M1	Surface low-iodide triple structure cubic grains	0.46	13	2.2
N1	Polydisperse twin crystal grains	0.72	25	1.5
01	Polydisperse tabular grains Aspect ratio 2.5	1.82	28	1.5

- 137 -

٠.

5

10

Table 5 Spectral sensitization of respective emulsions

Emulsion	Sensitizing dye added	Addition amount (10 <sup>-4</sup> mol/mol Ag)
A1	s1-1/s1-2	4.0/4.0
B1	S1-1/S1-2	4.0/4.0
C1	S1-1/S1-2	1.9/1.9
D1	S1-1/S1-2	1.7/1.7
E1	S1-1/S1-2	1.7/0.6
F1	S1-3/S1-4	6.0/0.6
G1	S1-3/S1-4	5.0/0.5
Н1	S1-3/S1-4	2.5/0.3
11	S1-4	5.0
J1	S1-4	3.0
K1	S1-5	3.2
L1	S1-5	4.1
M1	S1-5	3.0
N1	S1-5	1.7
01	S1-5	2.0

manner as for the sample B101 except that the couplers and red-sensitive emulsions contained therein and further red-sensitive layer coating amounts were changed as indicated in Table 6. Changing of couplers with respect to each of the color-sensitive layers was conducted in the following manner.

(Red-sensitive layer)

Couplers Cp-1, 2 were replaced by coupler CC-2 in a molar ratio of 0.5, and the coupler Cp-3 in a molar

ratio of 0.6. In accordance with the coupler replacement, the high-boiling organic solvent was replaced as indicated with respect to the sample A102 in Example-1.

Further, without changing the emulsion ratio of each of the layers, the emulsion coating amount was decreased to, relative to that of the sample B101, 0.8-fold with respect to the low-speed layer, 0.7-fold with respect to the medium-speed layer and 0.6-fold with respect to the high-speed layer.

(Green-sensitive layer)

-:·

5

10

15

20

**:** .

Coupler Cp-4 was replaced by a mixture (molar ratio: 1:1) of couplers MC-31, 32 in a molar ratio of 0.7, and each of the couplers Cp-5, 6, 7 in a molar ratio of 0.6. In accordance with the coupler replacement, high-boiling organic solvent Oil-A was added in a mass ratio of 0.20 to the total amount of couplers.

Further, without changing the emulsion ratio of each of the layers, the emulsion coating amount was decreased to, relative to that of the sample B101, 1.0-fold with respect to the low-speed layer, 0.8-fold with respect to the medium-speed layer and 0.6-fold with respect to the high-speed layer.

25 (Blue-sensitive layer)

Couplers Cp-8, 9 was replaced by coupler YC-46 in a molar ratio of 0.7, and the coupler Cp-10 in a molar

ratio of 0.9.

٠.

5

10

**.** 

Further, without changing the emulsion ratio of each of the layers, the emulsion coating amount was decreased to, relative to that of the sample B101, 0.8-fold with respect to both the low-speed layer and the high-speed layer.

The high-boiling organic solvent, additive, gelatin, etc. not listed in Table 6 are unchanged from those of the sample B101. Red-sensitive emulsions A2-E2 and A3-E3 were prepared in the same manner as for the emulsion A1-E1 except that the addition amounts of sensitizing dyes were changed as indicated in Table 7.

ç.

					Table 6	9 6				
			Ü	Coupler in	ä	ŭ	Coupler in		Cou	Coupler in
	Emulsion in		red-s	red-sensitive layer	layer	green-s	green-sensitive layer	layer	blue-sen	blue-sensitive layer
Sample	Red-sensitive	א ווושא (זוווו)	Low-	Medium-	High-	Low-	Medium-	High-	Low-	High-
	layer	€	speed	speed	peeds	peeds	speed	speed	Speed	Speed layer
			layer	layer	layer	layer	layer	layer	layer	
B101	A1, B1, C1, D1, E1	675	Cp-1,2	Cp-1,2	Cp-1,2,3	Cp-1,2 Cp-1,2 Cp-1,2,3 Cp-4,5,6,7 Cp-4,5,7 Cp-4,5,7	Cp-4,5,7	Cp-4,5,7	Cp-8	Cp-8,9,10
B102	A3, B3, C3, D3, E3	625	Cp-1,2	Cp-1,2	Cp-1,2,3	Cp-1,2 Cp-1,2,3 Cp-4,5,6,7 Cp-4,5,7 Cp-4,5,7	Cp-4,5,7	Cp-4,5,7	Cp-8	Cp-8,9,10
B103	A2, B2, C2, D2, E2	665	Cp-1,2	Cp-1,2	Cp-1,2,3	Cp-1,2 Cp-1,2,3 Cp-4,5,6,7 Cp-4,5,7 Cp-4,5,7	Cp-4,5,7	Cp-4,5,7	Cp-8	Cp-8,9,10
B104	A2, B2, C2, D2, E2	665	CC-2	CC-2	CC-2	Cp-4,5,6,7 Cp-4,5,7 Cp-4,5,7	Cp-4,5,7	Cp-4,5,7	Cp-8	Cp-8,9,10
B105	A2, B2, C2, D2, E2	665	CC-2	CC-2	CC-2	MC-31,32	MC-31,32 MC-31,32	MC-31,32	Cp-8	Cp-8,9,10
B106	A2, B2, C2, D2, E2	665	CC-2	CC-2	CC-2	MC-31,32	MC-31,32 MC-31,32	MC-31,32	YC-46	YC-46

 $\%\lambda$  max was measured at D = 0.5, 1.0, 1.5 and 2.0 to reveal that  $\lambda$  maxs at the respective densities were the same.

5

10

15

ç.

Table 7

	Tubic /	
Emulsion	Sensitizing dye added	Addition amount (10 <sup>-4</sup> mol/mol Ag)
	aye added	(10 -mol/mol Ag)
A2	S1-1/S1-2	2.0/6.0
B2	S1-1/S1-2	2.0/6.0
C2	S1-1/S1-2	1.0/3.0
D2	S1-1/S1-2	0.9/2.6
E2	S1-1/S1-2	0.9/1.5
А3	S1-2/S1-6	4.0/4.0
В3	S1-2/S1-6	4.0/4.0
C3	S1-2/S1-6	1.9/1.9
D3	S1-2/S1-6	1.7/1.7
E3	S1-2/S1-6	1.7/0.6

The thus obtained photosensitive materials were processed by the same procedure as in the image-forming method of item A above, thereby forming duplicate images.

#### C; Evaluation of color reproduction

Each of the samples A101, A102 was cut into 35 mm widths, formed into cartridge configuration, charged in a camera, used to shoot a Macbeth-made color checker chart, gray chart (chart of different-density 16-step pattern), flowers, landscape, etc., and subjected to the aforementioned development processing. The shooting was effected while changing filters at the shooting so as to realize a satisfactory gray balance at a visual density of 1.0 with respect to all the samples.

The thus obtained original images were irradiated with tungsten rays, printed on the samples B101 to B106

∹.

5

10

15

20

ę,

in combinations as indicated in Table 8, and developed to thereby obtain duplicates. With respect to shooting conditions, filter conditions capable of reproduction of a step of 1.0 density into neutral gray with the use of sample AlO1 as original and sample BlO1 for duplication were determined.

All the experiments were carried out under the above conditions.

Evaluation was made as to whether each step of density of obtained duplicate gray charts reproduces the original or as to whether the duplicate of color checker chart, flowers, landscape, etc. reproduces the original. The method of evaluation comprised a sensorial evaluation of obtained images. (Evaluation was conducted by ten persons engaged in image evaluation at the Ashigara Laboratory of Fuji Photo Film Co., Ltd. and five assistants for them. Each grader was given 10 marks and graded images, and the sore was averaged. The greater the score, the greater the image excellence.)

A summary of the obtained results is listed in Table 8.

Remarks 2	Comp.	Comp.	Comp.	Inv.	Inv.	Inv.	Inv.
Remarks 1		Gray became excessively brown	Gray became excessively brown				
Color reproducibility (hue, saturation)	0.9	6.3	4.1	8.5	9.1	7.6	7.6
Gray balance of duplicate images	6.3	0	0	9.4	9.5	9.6	9.6
Photosensitive material for forming duplicate images	B102	B101	B102	B103	B104	B105	. B106
Photosensitive Photos material criginal images duplica	A101	A102	A102	. A102	A102	A102	A102
Run No.	1	2	ъ	4	5	9	7

Table 8

÷.

It is apparent from Table 8 that duplicates of satisfactory gray balance and excellent color reproduction can be obtained according to the present invention.

#### 5 (Example-2)

25

~ં.

¥.

The following silver halide color photosensitive material for use as an original, Sample C101, was prepared

Preparation of Sample C101

Preparation of triacetylcellulose film 10 (i) Triacetylcellulose was dissolved (13 % by weight) by a common solution casting process in dichloromethane/methanol = 92/8 (weight ratio), and triphenyl phosphate and biphenyldiphenyl phosphate in a 15 weight ratio of 2:1, which are plasticizers, were added to the resultant solution so that the total amount of the plasticizers was 14 % to the triacetylcellulose. Then, a triacetylcellulose film was made by a band The thickness of the support after drying was process. 97  $\mu$  m. 20

(ii) Components of undercoat layer

The two surfaces of the triacetylcellulose film were provided with the following undercoating. Numbers represent weight contained per liter of an undercoat solution.

Gelatin 10.0 g
Salicylic acid 0.5 g

¥ .

	Glycerin 4.0	g	
	Acetone 700	mL	
	Methanol 200	mL	
	Dichloromethane 80	mL	
5	Formaldehyde 0.1	mg	
	Water to make 1.0	L	
	Coating of back layers		
	(iii) One surface of the undercoate	ed supp	ort was
	coated with the following back layers.		
10	1st layer		
	Binder: acid-processed gelatin		
	(isoelectric point: 9.0)	1.00	g
	Polymeric latex: PX-2		
	(average grain size: 0.1 $\mu$ m)	0.13	g
15	Polymeric latex: PX-4		
	(average grain size 0.2 $\mu$ m)	0.23	g
	Ultraviolet absorbent UX-1	0.030	g
	Ultraviolet absorbent UX-2	0.010	g
	Ultraviolet absorbent UX-3	0.010	g
20	Ultraviolet absorbent UX-4	0.020	g
	High-boiling organic solvent OilX-2	0.030	g
	Surfactant WX-2	0.010	g
	Surfactant WX-4	3.0	mg
	2nd layer		
25	Binder: acid-processed gelatin		
	(isoelectric point: 9.0)	3.10	g
	Polymeric latex: PX-4		

	(average grain size: 0.2 $\mu$ m)	0.11	g
	Ultraviolet absorbent UX-1	0.030	g
	Ultraviolet absorbent UX-3	0.010	g
	Ultraviolet absorbent UX-4	0.020	g
5	High-boiling organic solvent OilX-2	0.030	g
	Surfactant WX-2	0.010	g
	Surfactant WX-4	3.0	mg
	Dye DX-2	0.10	g
	Dye DX-10	0.12	g
10	Potassium sulfate	0.25	g
	Calcium chloride	0.5	mg
	Sodium hydroxide	0.03	g
	3rd layer		
	Binder: acid-processed gelatin		
15	(isoelectric point: 9.0)	3.30	g
	Surfactant WX-3	0.020	g
	Potassium sulfate	0.30	g
	Sodium hydroxide	0.03	g
	4th layer		
20	Binder: lime-processed gelatin		
	(isoelectric point: 5.4)	1.15	g
	1 : 9 copolymer of methacrylic acid	and	
	methylmethacrylate (average grain	size:	2.0 $\mu$ m)
		0.040	g
25	6 : 4 copolymer of methacrylic acid	and	
	methylmethacrylate (average grain	size:	2.0 $\mu$ m)
		0.030	g

·\$.

٠, ال

Surfactant WX-2 0.060 g
Surfactant WX-1 7.0 mg
Hardener HX-1 0.23 g

5

10

15

20

25

(iv) Coating of photosensitive emulsion layers

The following photosensitive emulsion layers were
coated on the opposite side of the support to the side
on which the back layers were coated to make Sample
C101. Numbers represent addition amounts per m<sup>2</sup> of the
coating surface. Note that the effects of added
compounds are not restricted to the described purposes.

The gelatin set forth below were those having molecular weight (weight average molecular weight) of 100,000 to 200,000. Contents of main metal ions were 2,500 to 3,000 ppm of calcium, 1 to 7 ppm of iron, and 1,500 to 3,000 ppm of sodium.

Gelatin having calcium content of 1,000 or less were also used in combination.

The organic compounds to be contained were prepared as emulsified dispersions containing gelatin (WX-2, Wx-3 and Wx-4 were used as surfactants). Each of the photosensitive emulsions and yellow colloidal silver were also prepared as gelatin dispersions. The thus prepared dispersions were mixed to prepare coating solutions so that the described addition amounts are obtained, and served to coating for respective layers. CpdX-H, -O, -P and -Q, dye DX-1, -2, -3, -5, -6, -8, -9 and -10, HX-1, PX-3 and FX-1 to -9 were dissolved in

water or a suitable water miscible organic solvent such as methanol, dimethylformamide, ethanol or dimethylacetamide, and added to the coating solutions for the respective layers.

The gelatin concentrations (weight of solid gelatin / coating liquid volume) of the thus prepared layers were in the range of 2.5% to 15%, pH's of the respective coating solutions were in the range of 5.0 to 8.5, and pAg's of the respective coating solutions containing silver halide emulsions were in the range of 7.0 to 9.5 when the pH's and temperatures thereof were adjusted to 6.0 and  $40^{\circ}\text{C}$ , respectively.

After the coating, the sample was obtained by drying steps of multiple stages in which the temperatures were maintained in the range of  $10^{\circ}\text{C}$  to  $45^{\circ}\text{C}$ .

1st layer: Antihalation layer

5

10

	Black colloidal silver	0.20	g
	Gelatin	2.20	g
20	Compound CpdX-B	0.010	g
	Ultraviolet absorbent UX-1	0.050	g
	Ultraviolet absorbent UX-3	0.020	g
	Ultraviolet absorbent UX-4	0.020	g
	Ultraviolet absorbent UX-5	0.010	g
25	Ultraviolet absorbent UX-2	0.070	g
	Compound CodX-F	0.20	g
	High-boiling organic solvent OilX-2	0.020	g

	High-boiling organic solvent OilX-6	0.020	g
	Dye DX-4	1.0	mg
	Dye DX-8	1.0	mg
	Fine crystal solid dispersion	0.05	g
5	of dye EX-1		
	2nd layer: Interlayer		
	Gelatin	0.4	g
	Compound CpdX-F	0.050	g
	Compound CpdX-R	0.020	g
10	Compound CpdX-S	0.020	g
	High-boiling organic solvent OilX-6	0.010	g
	High-boiling organic solvent OilX-7	5.0 r	ng
	High-boiling organic solvent OilX-8	0.020	g
	Dye DX-11	2.0	mg
15	Dye DX-7	4.0	mg
	3rd layer: Interlayer		
	Gelatin	0.4	g
	4th layer: Photosensitive emulsion layer		
	Emulsion RX silver	0.20	g
20	Emulsion SX silver	0.10	g
	Silver iodide emulsion grains (cubic	c grain	ns,
	av. equivalent sphere diameter 0.0	05µm)	
	silver	0.050	g
	Gelatin	0.5	g
25	Compound CpdX-F	0.030	g
	High-boiling organic solvent OilX-6	0.010	g

	5th	layer:	Phot	tose	nsitive	emuls	sion	layer		
		Emulsi	ion 1	UX			sil	ver	0.20	g
		Gelati	in						0.4	g
	6th	layer:	Inte	er l	ayer					
5		Gelati	in						1.50	g
		Compor	ınd (	CodX	M-M				0.10	g
		Compor	ınd (	CodX	K-D				0.010	g
		Compo	und (	CodX	K-K				3.0	mg
		Compo	und (	CodX	<b>C-O</b>				3.0 r	mg
10		Compo	und (	CodX	<b>X-T</b>				5.0 r	mg
		Ultra	viol	et a	absorben	t UX-	6		0.010	g
		High-l	ooil	ing	organic	solv	ent	OilX-6	0.010	g
		High-l	ooil	ing	organic	solv	ent	OilX-3	0.010	g
		High-	ooil	ing	organic	solv	ent	OilX-4	0.010	g
15	7th	layer:	Low-	-spe	ed red-s	sensi	tive	emulsi	on lay	yer
		Emuls	ion .	AX			sil	ver	0.15	g
		Emuls	ion :	BX			sil	ver	0.10	g
		Emuls	ion	CX			sil	ver	0.15	g
		Yello	W CO	lloi	idal sil	ver	sil	ver	1.0	mg
20		Gelat	in						0.60	g
		Couple	er.C	X-1					0.15	g
		Couple	er C	X-2					7.0 m	g
		Ultra	viol	et a	absorben	t UX-	2		3.0	mg
		Compo	und	CpdX	<b>⟨</b> −J				2.0	mg
25	_	High-	boil	ing	organic	solv	ent	OilX-5	0.050	g
		High-	boil	ing	organic	solv	ent	OilX-10	)	
									0.020	g

	8th 1	ayer	: Inter	laye	er						
		Emul	sion CX				silv	er		0.20	g
		Emul	sion DX				silv	er		0.15	g
		Inte	rnally	fogg	ged sil	ver	brom	ide e	emu	lsion	grains
5		(c	ubic gr	ains	s, aver	age	equi	vale	nt	spher	e
		di	ameter	0.11	lµm)		silv	er		0.010	g
		Gela	tin							0.60	g
		Coup	ler CX-	1						0.15	g
		Coup	ler CX-	·2						7.0 m	ıg
10		High	-boilir	ıg o	rganic	solv	rent	OilX·	-5	0.050	g
		High	-boilir	ıg o	rganic	solv	ent	OilX	-10		
										2.0 m	ıg
	9th 1	layer	: High-	spe	ed red-	sens	itiv	e emu	uls	ion l	ayer
		Emul	sion EX	<b>T</b>			sil	ver		0.15	g
15		Emul	sion F	Z			sil	ver		0.20	g
		Gela	tin							1.50	g
		Coup	oler CX-	-1						0.70	g
		Coup	oler CX-	-2						0.025	g
		Coup	oler CX-	-3						0.020	) g
20		Coup	oler CX-	-8						3.0 m	ng
		Ultr	aviolet	ab	sorbent	: UX-	-1			0.010	) g
		High	n-boilir	ng o	rganic	solv	rent	OilX	-5	0.25	g
		High	n-boilir	ng o	rganic	solv	vent	OilX	-9	0.05	g
		High	n-boilin	ng o	rganic	solv	rent	OilX	-10	)	
25										0.10	g
		Comp	ound C	odX-	D					3.0	mg
		Comp	oound C	odX-	L					1.0	mg

·		Compound CpdX-T	0.050 g
•		Additive PX-1	0.010 g
		Additive PX-3	0.010 g
		Dye DX-8	1.0 mg
5	10th	layer Interlayer	
		Gelatin	0.50 g
		Additive PX-2	0.030 g
		Dye DX-5	0.010 g
		Dye DX-9	6.0 mg
10		Compound CpdX-I	0.020 g
		Compound CpdX-O	3.0 mg
		Compound CpdX-P	5.0 mg
	11th	layer: Interlayer	
		Yellow colloidal silver silver	3.0 mg
15		Gelatin	1.00 g
		Additive PX-2	0.010 gʻ
		Compound CpdX-A	0.030 g
		Compound CpdX-M	0.10 g
		Compound CpdX-O	2.0 mg
20		Ultraviolet absorbent UX-1	0.010 g
		Ultraviolet absorbent UX-2	0.010 g
		Ultraviolet absorbent UX-5	5.0 mg
		High-boiling organic solvent OilX-3	3 0.010 g
		High-boiling organic solvent OilX-6	5 0.10 g
25		High-boiling organic solvent OilX-	LO
	12th	layer: Low-speed green-sensitive em	nulsion layer
		Emulsion GX silver	0.15 g

		Emulsion HX	silver	0.15 g	,
		Emulsion IX	silver	0.15 g	
		Gelatin		1.00 g	
		Coupler CX-4		0.060 g	
5		Coupler CX-5		0.10 g	
		Compound CpdX-B		0.020 g	
		Compound CpdX-G		2.5 mg	
		Compound CpdX-K		1.0 mg	
		High-boiling organic s	solvent OilX-2	0.010 g	
10		High-boiling organic s	solvent OilX-5	0.020 g	
	13th	layer: Medium-speed gr	reen-sensitive	emulsion la	yer
		Emulsion IX	silver	0.10 g	
		Emulsion JX	silver	0.20 g	
		Gelatin		0.50 g	
15		Coupler CX-4		0.10 g	
		Coupler CX-5		0.050 g	
		Coupler CX-6		0.010 g	
		Compound CpdX-B		0.020 g	
		Compound CpdX-U		8.0 mg	
20		High-boiling organic	solvent OilX-2	0.010 g	
		High-boiling organic	solvent OilX-5	0.020 g	
		Additive PX-1		0.010 g	
	14th	layer: High-speed gree	en-sensitive en	nulsion laye	er
		Emulsion JX	silver	0.15 g	
25		Emulsion KX	silver	0.25 g	

		Internally fog	ged silver	bromide emu	ulsion	grains
		(cubic grain	s, average	equivalent	sphere	9
		diameter 0.1	1μm)	silver	5.0 mg	j
		Gelatin			1.20	g
5		Coupler CX-4			0.50	g
		Coupler CX-5			0.20	g
		Coupler CX-7			0.10	g
		Compound CpdX-	В		0.030	g
		Compound CpdX-	·U		0.020	g
10		High-boiling o	rganic solv	ent OilX-5	0.15	g
		Additive PX-1			0.030	g
	15th	layer: Yellow	filter laye	r		
		Yellow colloid	lal silver	silver	2.0 n	mg
		Gelatin			1.0	g
15		Compound CpdX-	-C		0.010	g
		Compound CpdX-	·M		0.020	g
		High-boiling o	organic solv	ent OilX-1	0.020	g
		High-boiling o	organic solv	ent OilX-6	0.020	g
		Fine crystal s	solid disper	sion	0.25	g
20		of dye EX-2				
	16th	layer: Photose	nsitive emu	lsion layer	2	
		Emulsion TX		silver	0.15	g
		Gelatin			0.40	g
		Coupler CX-1				mg
25		Coupler CX-2				mg
		High-boiling o	organic solv	rent OilX-5		mg
		Compound CpdX-	-Q		0.20	g

		Dye DX-6		2.0 mg
	17th	layer: Low-speed blue-sen	sitive emul	lsion layer
		Emulsion LX	silver	0.10 g
		Emulsion MX	silver	0.10 g
5		Emulsion NX	silver	0.10 g
		Internally and surface for	ogged silve	r bromide
		emulsion grains (cubic	grains, av	erage
		equivalent sphere diame	eter 0.11µm	)
			silver	0.010 g
10	•	Gelatin		0.80 g
		Coupler CX-8		0.020 g
		Coupler CX-9		0.020 g
		Coupler CX-10		0.20 g
		Compound Cpd-B		0.010 g
15		Compound Cpd-I		8.0 mg
		Compound Cpd-K		2.0 mg
		Ultraviolet absorbent UX-	-5	0.010 g
		Additive PX-1		0.020 g
	18th	layer: Medium-speed blue-	-sensitive	emulsion layer
20		Emulsion NX	silver	0.20 g
		Emulsion OX	silver	0.20 g
		Gelatin	•	0.80 g
		Coupler CX-8		0.030 g
		Coupler CX-9		0.030 g
25		Coupler CX-10		0.30 g
		Compound CpdX-B		0.015 g
		Compound CpdX-E		0.020 g

		Compound CpdX-N		2.0 m	ng
		Compound CpdX-T		0.010	g
		Ultraviolet absorbent UX-	5	0.015	g
		Additive PX-1		0.030	g
5	19th	layer: High-speed blue-ser	nsitive emu	ılsion	layer
		Emulsion PX	silver	0.20	g
		Emulsion QX	silver	0.15	g
		Gelatin		2.00	g
		Coupler CX-8		0.10	g
10		Coupler CX-9		0.15	g
		Coupler CX-10		1.10	g
		Coupler CX-3		0.010	g
		High-boiling organic solv	ent OilX-5	0.020	g
		Compound CpdX-B		0.060	g
15		Compound CpdX-D		3.0 r	ng
		Compound CpdX-E		0.020	g
		Compound CpdX-F		0.020	g
		Compound CpdX-N		5.0 r	mg
		Compound CpdX-T		0.070	g
20		Ultraviolet absorbent UX-	5	0.060	g
		Additive PX-1		0.10	g
	20th	layer: 1st protective lay	er		
		Gelatin		0.70	g
		Ultraviolet absorbent UX-	1	0.020	g
25		Ultraviolet absorbent UX-	5	0.030	g
		Ultraviolet absorbent UX-	2	0.10	g
		Compound CpdX-B		0.030	g

•		Compound CpdX-O	5.0 n	ng
		Compound CpdX-A	0.030	g
		Compound CpdX-H	0.20	g
		Dye DX-1	2.0	mg
5		Dye DX-2	3.0	mg
		Dye DX-3	2.0	mg
		High-boiling organic solvent OilX-2	0.020	g
		High-boiling organic solvent OilX-3	0.030	g
	21st	layer: 2nd protective layer		
10		Silver iodobromide emulsion grains	(avera	ge
	equiv	valent sphere diameter 0.06 μm, silve	er iodi	ide
	conte	ent: 1 mol%)		
		silver	0.10	g
		Gelatin	0.80	g
15		Ultraviolet absorbent UX-2	0.030	g
		Ultraviolet absorbent UX-5	0.030	g
		High-boiling organic solvent OilX-2	0.010	g
	22nd	layer: 3rd protective layer		
		Gelatin	1.00	g
20		Polymethylmethacrylate		
		(average grain size 1.5μm)	0.10	g
		6: 4 copolymer of methylmethacryla	te and	
		methacrylic acid (average grain s	ize 1.	5µm)
			0.15	g
25		Silicone oil SOX-1	0.20	g
		Surfactant WX-1	0.010	g
		Surfactant WX-2	0.040	g

In addition to the above compositions, additives FX-1 to FX-9 were added to all emulsion layers. Also, a gelatin hardener HX-1 and surfactants WX-2, WX-3, and W-4 for coating and emulsification were added to each layer.

Furthermore, phenol, 1,2-benzisothiazoline-3-one, 2-phenoxyethanol, phenethylalcohol, and p-benzoic butylester were added as antiseptic and mildewproofing agents.

Sample C101 prepared as above had a coating film thickness at dry state of 25.8 $\mu m$ , and a swelling ratio when swelled with purified water at 25°C was 1.78 times.

Table 9 Constitution of silver halide emulsions AX-UX

Av. AgI halide content composition content composition surface (1) (2) (3) (4) halide grains (mol%) of silver (mol%) a.5 structure (mol%) a.5 structure at grain structure at grain (mol%) a.5 structure at grain (mol%) a.5 structure at grain at grain at grain (mol%) a.5 structure at grain at grain at grain (mol%) a.5 structure at grain at grain at grain (mol%) a.5 structure at grain at gra	Silver iodobromide emulsion used in	lver iodob	입	rom	ide emuls	ion used in Sa	Sample C101	1			†	
Av. ESD         COV content composition (#m)         at grain (mol%) content composition surface (mol%)         at grain (mol%) (mol%)         (mol%) (mol%)         (mol%)         (4)           0.18         10         3.5         Triple 2.5         2.5         O         O         O         O           0.20         10         2.5         structure 2.5         0.1         O					1	Structure in	AgI content	Other		aract	erist	ics
0.18 10 3.5 Triple 2.5 0 0 0 0 0 0 0 0.20 10 2.5 structure 2.5 0.1 0 0 0 0 0 0.32 11 1.8 Triple 2.0 0.1 0 0 0 0 0.32 21 4.8 Triple 2.0 0 0 0 0 0 0.48 12 0 0 0 0 0 0 0 0 0.65 12 1.6 Triple 0.6 0.3 0 0 0 0 0 0.22 12 1.9 Quadruple 0.7 0 0 0 0 0 0.22 12 1.9 Quadruple 0.7 0 0 0 0 0 0.35 12 3.5 Structure 2.5 0 0 0 0 0 0.35 12 3.5 Structure 2.5 0 0 0 0 0 0.35 12 3.5 Structure 2.5 0 0 0 0 0 0 0.35 12 3.5 Structure 2.5 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	Characteristics	S	Av. ESD (μm)	COV (%)	Av. Agi content (mol%)	halide composition of silver halide grains	at grain surface (mol%)	(1)	(2)	(3)	(4)	(5)
0.20         10         2.5         Quadruple structure         2.5         0         0           0.32         11         1.8         Triple structure         2.0         0         0           0.48         12         0         Quadruple structure         1.3         0         0           0.65         12         1.6         Triple structure         0.6         0         0         0           0.14         9         3.5         Quadruple structure         0.7         0         0         0           0.22         12         1.9         Quadruple structure         0.7         0         0         0           0.35         12         3.5         Quintuple structure         1.5         0         0         0	Monodisperse tetradecahedral grains	ains	0.18	10	3.5	Triple structure	2.5	0	0		0	
0.32       11       1.8       Triple structure       0.1       0       0         0.32       21       4.8       Triple structure       2.0       0       0         0.48       12       0       Quadruple structure       0.6       0       0       0         0.14       9       3.5       Quadruple structure       0.3       0       0       0         0.22       12       1.9       Quadruple structure       0.7       0       0       0         0.35       12       3.5       Quintuple structure       1.5       0       0       0	Monodisperse (111) tabular grains Av. aspect ratio3.0	bular .0	0.20	10	2.5	Quadruple structure	2.5		·	0		0
0.32         21         4.8         Triple structure         2.0         O <td>Monodisperse (111) tabular grains Av. aspect ratio4.5</td> <td>ular 5</td> <td>0.32</td> <td>11</td> <td>1.8</td> <td>Triple</td> <td>0.1</td> <td></td> <td>0</td> <td></td> <td>0</td> <td>0</td>	Monodisperse (111) tabular grains Av. aspect ratio4.5	ular 5	0.32	11	1.8	Triple	0.1		0		0	0
0.48         12         0         Quadruple structure         1.3         O         P         P           0.65         12         1.6         Triple structure         0.6         O	Monodisperse (111) tabul grains Av. aspect ratio6.0	ılar )	0.32	21	4.8	Triple structure	2.0		0		0	0
0.65       12       1.6       Triple structure       0.6       0.9       0       0         0.14       9       3.5       Quadruple structure       0.3       0	Monodisperse (111) tabular grains Av. aspect ratio6.0	lar	0.48	12	0	Quadruple structure	1.3		0			
0.14         9         3.5         Quadruple structure         0.3         O         O         O           0.22         12         1.9         Quadruple structure         0.7         O         O         O           0.35         12         3.5         Quintuple structure         1.5         O         O         O	Monodisperse (111) tabular grains Av. aspect ratio8.0	lar	0.65	12	1.6	Triple structure	9.0		0	0		0
0.22 12 1.9 Quadruple 0.7 O O 0.35 12 3.5 Quintuple 1.5 O O	Monodisperse cubic grains	ains	0.14	6	3.5	Quadruple structure	0.3	0		0	0	
0.35 12 3.5 Quintuple 1.5 O O O O O	Monodisperse cubic grains	ains	0.22	12	1.9	Quadruple structure	0.7		0			0
	Monodisperse (111) tabular grains Av. aspect ratio4.0	ular O	0.35	12	3.5	Quintuple structure	1.5	0	0		0	0

(Continued)

	,,			_			_		<u> </u>				-	16	50		-					<u> </u>			γ .		
	characteristics			<u>(c)</u>			0			0			)							0			0			0	
	teris			f 			0								) 					0							
	arac			် (၁)						0		C	)				0			0							<u> </u>
				(7)			0			0				(	)		0			0			0			0	
	Other		-	Ŧ)	_					0							0						0			0	
Sample C101	TAG	at concent	ac granii	Surrace (mol*)	(87011)		2.2			1.3		o	0.0	u G	6.2		4.0			1.0		u C	r. >			0.5	
emulsion used in S	Structure in	halide	composition	of silver	halide grains	- [	Quadrupie	structure	E	ardıı	stractare	Triple	structure	Triple	structure	ر الروزية من الروزية ا	Quincuple	stractare	, Lander 10	Adaut upre	structure	E	erdri	srinciare	0	Quadrupie	structure
		Av. AgI	content	(mol%)			2.0			1.7		7 6	٠٠,	2 6	6.7		2.1			2.5			2.8			1.0	
iodobromide		VON	) (a)	(0)			21			13		d	9	O	y		13		!	თ			21			ω	
Silver iod		AV. ESD	( "")				0.40			0.65		000	0.00	Ċ	0.30		0.35			0.45			0.70			0.85	
Si			Characteristics			Monodisperse (111) tabular	grains	Av. aspect ratio7.0	Monodisperse (111) tabular	grains	Av. aspect ratio 8.5	Monodisperse	tetradecahedral grains	Monodisperse	tetradecahedral grains	Monodisperse (111) tabular	grains	Av. aspect ratio 3.0	Monodisperse (111) tabular	grains	Av. aspect ratio 5.0	Monodisperse (111) tabular	grains	Av. aspect ratio 9.0	Monodisperse (111) tabular	grains	Av. aspect ratio 9.0
		_	Emulsion				χ̈́ς			X.	•	X:	VI.	NA.	VIJ		NX			xo			PX			Xŏ	

Table 9

			ics		(2)		0			0			0			0	
			Other characteristics		(2) (3) (4) (5)		•										
			aract		(3)					0						0	
			r che		(2)		0			0			0			0	
			Othe		(1)		0						0				
	ample C101	AgI	content at	grain	surface (mol%)		4.0			3.0			2.8			1.5	
	Silver iodobromide emulsion used in Sample C101	Structure in	halide	composition	of silver halidegrains	)   wind or 10	Quadiupie	Stucture	واطنطودنان	Quadrupte	Stactate	واعتصاحتين	grantubie	SCIUCCUIE	Птіп	etrictire	Structure
e 9	ide emuls	1	Av. AgI	content	(mol%)		8.0			12.5			10.5			12.5	
Table 9	oprom		COV	3	æ		15			13			13			15	
	llver iod		AV FSD		(m <b>x</b> )		0.40			0.70			0.45			0.55	
	S			Characteristics		Monodisperse (111)	tabular grains	Av. aspect ratio 5.0	Monodisperse (111)	tabular grains	Av. aspect ratio 4.0	Monodisperse (111)	tabular grains	Av. aspect ratio 4.0	Monodisperse (111)	tabular grains	Av. aspect ratio 4.0
				Emulsion			XX			SX XX			TX			Χn	

·°.

= Coefficient of variation Av. ESD = Equivalent-sphere average grain size; COV

(Other characteristics)

The mark "O" means each of the conditions set forth below is satisfied.

- A reduction sensitizer was added during grain formation;
- (2) A selenium sensitizer was used as an after-ripening agent
  - (3) A rhodium salt was added during grain formation.
- (4) A shell was provided subsequent to after-ripening by using silver nitrate in an amount of 10%, in terms of silver molar ratio, of the emulsion grains at that time, together with the equimolar amount of potassium bromide
  - (5) The presence of dislocation lines in an average number of ten or more per grain was observed by transmission electron microscope.

Note that all the lightsensitive emulsions were after-ripped by the use of sodium thiosulfate, sodium thiocyanate, and sodium aurichloride. Note, also, a iridium salt was added during grain formation.

Note, also, that chemically-modified gelatin whose amino groups were partially converted to phthalic acid amide, was added to emulsions BX, CX, EX, HX, JX, NX, QX, RX, SX, and TX. ٠.,

Emulsions AX - PX	Timing of adding sensitizing dye	Subsequent to after-ripening	Prior to after-ripening	Subsequent to after-ripening	Subsequent to after-ripening	Prior to after-ripening	Subsequent to after-ripening	Subsequent to after-ripening	Prior to after-ripening	Subsequent to after-ripening	Prior to after-ripening	Prior to after-ripening													
Spectral sensitization of	Addition amount per mol of silver halide (g)	0.75	0.15	0.10	0.60	0.30	0.05	0.60	0.20	0.07	0.70	0.15	0.10	0.75	0.30	0.15	0.90	0.30	0.15	0.65	0.10	0.60	0.10	0.70	0.10
Table 10	Sensitizing dye added	SX-1	SX-2	SX-3.	SX-1	SX-2	SX-3	SX-1	SX-2	SX-3	SX-1	SX-2	SX-3	SX-1	SX-2	SX-3	SX-1	SX-2	SX-3	SX-4	SX-5	SX-4	SX-5	SX-4	SX-5
	Emulsion		AX			ВХ			χ			ΧO			EX			FX		ò	Vo.	λH	WII	<u>}</u>	٧٦

(Continued)

		Table 10	
Emulsion	Sensitizing dye added	Addition amount per mol of silver halide (g)	Timing of adding sensitizing dye
	5X-4	0.70	Prior to after-ripening
ጵ	SX-5	0.10	Subsequent to after-ripening
	SX-6	0.08	Subsequent to after-ripening
	SX-4	0.70	af
X	SX-5	0.15	Prior to after-ripening
	8X-6	0.10	Prior to after-ripening
	9-XS	0.10	Subsequent to after-ripening
LX, MX	SX-7	0.10	Subsequent to after-ripening
	SX-8	0.50	ţ٥
	9-XS	0.10	ಭ
XN	SX-7	0.15	Subsequent to after-ripening
	SX-8	0.55	Subsequent to after-ripening
<b>^</b> O	L-XS	0.20	Subsequent to after-ripening
Š .	SX-8	0.65	Subsequent to after-ripening
	8X-6	0.06	to
PX	SX-7	0.15	Subsequent to after-ripening
	SX-8	0.70	Subsequent to after-ripening
	SX-6	0.05	Prior to after-ripening
ΧŎ	SX-7	0.15	Prior to after-ripening
	8X-8	0.80	Prior to after-ripening
>0	SX-4	0.40	Subsequent to after-ripening
W	SX-6	0.30	Subsequent to after-ripening
> 0	SX-4	0.40	Subsequent to after-ripening
VC	SX-6	0.30	Prior to after-ripening
ΧĿ	L-XS	0.05	Prior to after-ripening
WT.	8X-8	09.0	Prior to after-ripening
XII	SX-1	09.0	Prior to after-ripening
400	SX-3	0.30	Prior to after-ripening

C X - 3

C X - 4

$$NHCOC_3F_7$$
 $NHCOC_3F_7$ 
 $NHCOC_3F_7$ 

CX-9 CX-10 CX-

OilX-1 OilX-2 Tricresyl phosphate Tri(n-hexyl)phosphate 5 OilX-4 oilx-3 Tricyclohexyl phosphate 10 OilX-6 OilX-5 Ç<sub>6</sub>H<sub>13</sub>(n) C<sub>8</sub>H<sub>17</sub>(n) CONH<sub>2</sub> oilx-7 OilX-8 15 (A mixture of isomers) OilX-9 (t)C<sub>8</sub>H<sub>17</sub> 20 OilX-10

CpdX-A

CpdX-D

CpdX-B

 $C_3H_7O$ 

C<sub>3</sub>H<sub>7</sub>O

ŞO₂Na COOC<sub>14</sub>H<sub>29</sub>(n) (n)C<sub>14</sub>H<sub>29</sub>OOC

сн₃

H<sub>3</sub>C

H<sub>3</sub>C

∠CH<sub>3</sub>

OC<sub>3</sub>H<sub>7</sub>

CpdX-EH₃C、 ОН ∠CH<sub>3</sub> H<sub>3</sub>C√

C<sub>2</sub>H<sub>5</sub>OOC OC<sub>16</sub>H<sub>33</sub>(n)

CpdX-G

C p d X – G
$$C_4H_9 \longrightarrow C_2H_5$$

$$(n)C_{16}H_{33}O$$

CpdX-H

CpdX-F

15

$$CpdX-K$$

### 5 CpdX-L

# CpdX-N

### CpdX-P

$$CpdX-R$$

C p d X 
$$-$$
 M OH  $C_8H_{17}(n)$   $C_6H_{13}(n)$ 

### CpdX-O

### CpdX-Q

### CpdX-S

15

CpdX-T

5 U X — 1

$$\begin{array}{c|c} & H_3C \\ & HO \\ & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

 $\begin{array}{c} \text{U X} - \text{3} \\ \text{CI} \\ \\ \text{C}_4 \text{H}_9(\text{t}) \\ \\ \text{C}_4 \text{H}_9(\text{t}) \end{array}$ 

U X — 5

10

CpdX-U

 $\begin{array}{c|c} UX-2 \\ \hline \\ OC_4H_9 \\ \hline \\ C_4H_9O \\ \end{array}$ 

U X -4HO  $C_4H_9(t)$ 

 $\begin{array}{c} \text{U X} - 6 \\ \text{CI} \\ \\ \text{N} \\ \\ \text{N} \\ \end{array}$ 

# sx-2

# 5 s x - 3

# **S** X – 4

### 10 **SX-5**

$$\begin{array}{c} \text{S X} - 6 \\ \\ H_{3}\text{CO} \\ \\ \downarrow \\ \text{SO}_{3} \\ \\ \text{SO}_{3} \\ \\ \text{SO}_{3} \\ \\ \text{H}_{3}\text{C} \\ \\ \text{SO}_{3} \\ \\ \text{H}_{3}\text{C} \\ \\ \text{SO}_{3} \\ \\ \text{SO}_{3} \\ \\ \text{H}_{4}\text{C} \\ \\ \text{SO}_{3} \\ \\ \text{H}_{5}\text{C} \\ \\ \text{SO}_{3} \\ \\ \text{H}_{7}\text{C} \\ \\ \text{SO}_{3} \\ \\ \text{H}_{7}\text{C} \\ \\ \text{SO}_{3} \\ \\ \text{H}_{7}\text{C} \\ \\ \text{SO}_{3} \\ \\ \text{H}_{8}\text{C} \\ \\ \text{SO}_{3} \\ \\ \text{H}_{8}\text{C} \\ \\ \text{SO}_{3} \\ \\ \text{H}_{8}\text{C} \\ \\ \text{SO}_{3} \\ \\ \text$$

D X - 1

D X — 2

D X - 3

D X - 4

$$\begin{array}{c} C_5H_{11}(t) \\ CONH(CH_2)_3O \\ \hline \\ CH_3 \\ \hline \\ C_2H_5 \\ \hline \\ C_2H_5 \\ \end{array}$$

$$DX-6$$

$$\begin{array}{c|c} X-7 & C_2H_5 \\ \hline 0 & NH & C_2H_5 \\ \hline 0 & NH & C_2H_5 \\ \hline \end{array}$$

# D\_X \_ 8

$$\begin{array}{c|c} OH & CONHC_{12}H_{25} \\ \hline \\ OCH_2CH_2O & -N=N & OH & NHCOCH_3 \\ \hline \\ SO_3Na & SO_3Na \\ \end{array}$$

### D X — 9

$$\begin{array}{c|c} C_2H_500\cdot C \\ N \\ N \\ O \end{array} \begin{array}{c} CH-CH=CH-CH=CH\\ HO \\ N \\ N \\ SO_3K \\ \end{array} \begin{array}{c} COOC_2H_5 \\ SO_3K \\ \end{array}$$

# D X - 1 0

# DX-11

E X - 1

HOOC 
$$\longrightarrow$$
  $N$   $\stackrel{N}{\underset{H}{\bigvee}}$   $O$   $OH$   $\stackrel{CH_3}{\underset{H}{\bigvee}}$   $N$   $\stackrel{N}{\longrightarrow}$   $O$   $OOH$ 

E X - 2

HX-1

$$\begin{array}{l} {\rm CH_2}\!=\!{\rm CH}\!=\!{\rm SO_2CH_2CONH}\!-\!{\rm CH_2} \\ {\rm CH_2}\!=\!{\rm CH}\!=\!{\rm SO_2CH_2CONH}\!-\!{\rm CH_2} \end{array}$$

ŠO<sub>2</sub>Na

$$\begin{array}{c|c} FX-1 \\ \hline CH_3 & N & N \\ \hline OH \\ \hline FX-3 & N & SH \\ \hline N & N & SH \\ \hline \end{array}$$

F X 
$$-$$
 2

N NH (CH<sub>2</sub>)  $_3$ NH
HN0 $_3$ 
NHCH<sub>2</sub>CH<sub>2</sub>OH
 $_2$ OH
 $_2$ OH
 $_3$ 

F X - 9

FX-8

$$HS \longrightarrow N$$

NHCOCHC<sub>4</sub>H

$$N-N$$

SOX-1

F X - 7

$$\begin{array}{c|c} \text{(CH}_3)_3 \text{SiO} & \begin{array}{c} \text{CH}_3 \\ \text{Si} \\ \end{array} \\ \begin{array}{c} \text{CH}_3 \\ \text{Si} \\ \end{array} \\ \begin{array}{c} \text{CH}_3 \\ \text{Si} \\ \end{array} \\ \begin{array}{c} \text{CH}_3 \\$$

Preparation of organic solid dispersed dye

(Preparation of fine crystalline solid dispersion of dye EX-1)

5

10

15

20

25

100 g of Pluronic F88 (an ethylene oxide-propylene oxide block copolymer) manufactured by BASF CORP. and water were added to a wet cake of the dye EX-1 (the net weight of EX-1 was 270 g), and the resultant material was stirred to make 4,000 g. Next, the Ultra Visco Mill (UVM-2) manufactured by Imex K.K. was filled with 1,700 mL of zirconia beads with an average grain size of 0.5 mm, and the slurry was milled through this UVM-2 at a peripheral speed of approximately 10 m/sec and a discharge rate of 0.5 L/min for 2 hr. The beads were filtered out, and water was added to dilute the material to a dye concentration of 3%. After that, the material was heated to 90°C for 10 hr for stabilization. The average grain size of the obtained fine dye grains was 0.30 mm, and the grain size distribution (grain size standard deviation X 100/average grain size) was 20%.

(Preparation of fine crystalline solid dispersion of dye EX-2)

Water and 270 g of W-4 were added to 1,400 g of a wet cake of EX-2 containing 30 weight% of water, and the resultant material was stirred to form a slurry having an EX-2 concentration of 40 weight%. Next, the Ultra Visco Mill (UVM-2) manufactured by Imex K.K. was

filled with 1,700 mL of zirconia beads with an average grain size of 0.5 mm, and the slurry was milled through this UVM-2 at a peripheral speed of approximately 10 m/sec and a discharge rate of 0.5 L/min for 8 hr. This dispersion was diluted to 20 weight% by ion exchange water to obtain a fine crystalline solid dispersion of Dye EX-2. The average grain size was 0.15 um.

5

10

15

20

25

Photographing was performed using this Sample C101 as a photosensitive material for use as an original, and Samples B103 and B106 were used as photosensitive material for use as a duplicate to conduct the same evaluation as in Example-1.

Good results as in Example-1 were obtained also in the duplicate by this method.

According to the method of the present invention, duplicated color images with improved saturation and gradation reproduction were able to be obtained.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative embodiments shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.